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Materials and Devices for Thermal-to-Electric Energy Conversion

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Symposium N was the ninth in a series of state-of-the-art materials and technologies for direct thermal-to-electric energy conversion symposia with primary focus on material and technological advances of thermoelectric and thermionics. In this symposium there were 93 contributed presentations, including 17 invited talks and 28 poster presentations. These presentations showed the continuing technological development in thermal-to-electric energy conversion from research in academia, national laboratories, and industry in the United States, Asia and Europe. The symposium covered a broad range of topics in the areas of materials, devices, and applications. The tutorial session was led by Dr. Thierry Caillat of NASA Jet Propulsion Laboratory, Mr. Francis Stabler of Future Technologies, and Dr. Ryoji Funahashi of the National Institute of Advanced Industrial Science and Technology, Japan, and covered space, automotive, and industrial applications of thermoelectric technology. Harald Boettner, Fraunhofer Institute for Physical Measurement Techniques, began the symposium with an overview of the state-of-the-art in high-temperature thermoelectric materials. Dr. Boettner's talk covered materials cost, manufacturability, availability, etc., in addition to their thermoelectric properties, which provide important insights on material choices for technology development. The symposium session on nanocomposite materials included an overview given by Mildred Dresselhaus, MIT, on bulk nanostructured materials, on the of the recent intensively investigated areas in the thermoelectric community. Peter Rogel, University of Vienna, gave an overview on the potential of inverse clathrates for thermoelectric applications. Continued interest in the area of thermoelectric was evidenced by the excellent level of attendance throughout the symposium.

As with previous symposia in this series, there were a large number of graduate student presentations. This continues to be a focus of our symposium, emphasizing the strong interest from our future scientists in this field of materials research. With the generous support of the symposium sponsors, the organizers were able to give presentation awards to six students:

Oral Presentations

- Reja Amatyia, MIT, "Materials for Solar Thermoelectric Generators"
- Sabah Bux, UCLA, "High Temperature Thermoelectric Properties of Nano-Bulk Silicon"
- Steven N. Girard, Northwestern, "Investigation of Solid-State Immiscibility and Thermoelectric Properties of the Systems PbTe-SnTe-PbS"
- Matthew Beckman, Univ of South Florida, "Preparation and Fundamental Properties of Clathrate-II Intermetallic Phases: Materials with Potential for Energy Conversion Applications"

Poster Presentations

- Tomomi Okada, Tokyo University of Science, "Preparation of Delafossite CuYO_2 by Metal-citric Acid Complex Decomposition Method"
- Takashi Nemot, Tokyo University of Science, "Output Power Characteristics of Mg_2Si and the Fabrication of Mg_2SiTe Module with a Unileg Structure"

The organizers are most grateful for the support of the U.S. Office of Naval Research and ULVAC Technologies, Inc. This support funded the student awards and allowed for travel funds to help support our contributing presenters.

Symposium N Organizers

Jihui Yang, General Motors R&D Center
George S. Nolas, University of Southern Florida
Kunihito Koumoto, Nagoya University, Japan
Yuri Grin, Max-Planck-Institute for Chemical Physics of Solids, Germany



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Symposium N: Materials and Devices for Thermal-to-Electric Energy Conversion

April 13 - 17, 2009

Chairs

Jihul Yang
Materials and Processes
Laboratory
General Motors R&D Center
Warren, MI 48090
586-986-9789

Kunihito Koumoto
Dept. of Applied Chemistry
Nagoya University
Nagoya, 464-8603 Japan
81-52-789-3327

George S. Nolas
Dept. of Physics
University of South Florida
Tampa, FL 33620
813-974-2233

Yuri Grin
Max-Planck-Institute for Chemical Physics of
Solids
Noethnitzer Str. 40
Dresden, D-01187 Germany
49-351-4646-4000



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* Invited paper

TUTORIAL

Applications of Thermoelectric Technology

Monday, April 13
1:30 PM - 5:00 PM
Room 2010, Moscone West

Historically, thermoelectric technology has only occupied niche areas, such as the radioisotope thermoelectric generators for NASA's spacecrafts, where the low-cooling coefficient of performance (COP) and energy-conversion efficiency are outweighed by the application requirements. Recent materials advances and an increasing awareness of energy and environmental conservation issues have rekindled prospects for many applications of thermoelectric technology. The intention of the tutorial is to give the attendee an overview of thermoelectric energy-conversion technology for radioisotope space power systems and new concept of novel oxides for power generation purposes.

Instructors:
Thierry Caillat

Jet Propulsion Laboratory, California Institute of Technology

Francis R. Stabler
Future Tech LLC

Ryoji Funahashi
National Institute of Advanced Industrial Science & Technology, Japan

SESSION N1: Applications and Devices
Chairs: David Johnson and Jihui Yang
Tuesday Morning, April 14, 2009
Room 2010 (Moscone West)

9:00 AM *N1.1

Thermoelectrics for High Temperatures: A Survey of State of the Art. Harald Boettner, TES, Fraunhofer Institute for Physical Measurement Techniques, Freiburg, Germany.

Energy is a scarce resource. Nevertheless, heat can be found escaping unused wherever you look. Around 60 percent of all fossil primary energy is converted into unused waste heat. Thermogenerators (TEGs) are known to be able to use those otherwise forever lost treasures of our earth. This makes thermoelectric generators useful assistants in the process known as energy harvesting. Converting heat into electrical energy using car waste heat will be not only a vision was demonstrated by the preliminary system presented by e.g. BMW during summer 2008. Fuel economy improvement of 5-8% for highway driving was reported by BMW. To enable this technology for exploiting waste heat and thus contribute to a more efficient utilization of natural resources, thermoelectric materials and standardized so called high temperature modules for high temperature differences - 500° C or even more - are a prerequisite. They must be easily accessible like today's Bi₂Te₃-based standard modules. To achieve this goal much effort is under way worldwide. Here a survey of the state of the art published development of high temperature materials is presented and the development in comparison to the well known situation in the 90th of the last century will be presented. An attempt will be made to assess state of art concerning thermoelectric properties, technical level, and possible potential for standard device technology. Also a first assessment based on the current commodity prices of elements of some important thermoelectric compounds will be made. For some compounds a survey will be given concerning advantages and drawbacks. Only if highly efficient, cost-effective TEGs for high temperatures will be commonly available, waste heat in automobiles or in large-scale industrial plants, such as furnaces and refuse incinerators can be converted into usable energy. Then thermoelectrics, as a recycler of "nomadic" energy supplies, could play an important role in complementing renewable energies as a complementary technology.

9:30 AM N1.2

Fabrication and Testing of Skutterudite-based, Thermoelectric Devices for Power Generation. Jeffrey Sakamoto, CHEMS, MSU, East Lansing, Michigan.

MSU and JPL are engaged in a collaborative effort to develop the next generation thermoelectric power generators for terrestrial waste heat recovery. This project is sponsored by the DOE EERE Program to improve fuel efficiency of commercial and passenger vehicles. The emphasis has primarily been on thermoelectric technology employing Skutterudite-based technology, which also includes segmenting with heritage materials such as TAGS and Bi₂Te₃. This work entails scaled-synthesis of n and p type Skutterudite powders, mass-production of metallized legs, module-bonding technology and thermoelectric subassembly integration into prototypical generators. Two thermoelectric generators are under consideration. First, a traditional design is under consideration whereby heat is extracted from the periphery of an exhaust component. The second design is enabled by aerogel-based thermal insulation, which integrates the thermoelectric elements inside an exhaust component giving direct access to high temperature exhaust gas. Finally, preliminary power output validation for >10Watt Skutterudite subassemblies will be presented.

9:45 AM N1.3

>10% Single-Stage and >13% Two-Stage Conversion Devices for Increased Fuel Efficiency In Portable Generator

Systems Chris Caylor¹, Rama Venkatasubramanian¹, Paul Dev², Chris Howells³ and Selma Matthews³; ¹RTI International, Research Triangle Park, North Carolina; ²D-STAR Engineering, Shelton, Connecticut; ³U.S. Army CERDEC, Ft. Belvoir, Virginia.

The development of single- and multi-stage thermoelectric devices for high conversion efficiencies will be reported. Single-stage devices consisting of n-PbTe and p-TAGS elements have demonstrated >10% conversion efficiencies with $T_{hot} \sim 450^{\circ}\text{C}$ and $T_{cold} \sim 25^{\circ}\text{C}$. Data from experiments using a Q-meter test apparatus will show a matrix of power and conversion efficiencies with T_{hot} from 400°C to 500°C and T_{cold} from 25°C to 150°C to cover a broad range of thermal management scenarios on the cold-side of the device. For example, >10% conversion efficiency is achieved for $T_{hot} \sim 450^{\circ}\text{C}$ and $T_{cold} \sim 25^{\circ}\text{C}$, as stated above, however, >10% is achieved with cold-side temperature as high as $\sim 75^{\circ}\text{C}$ with $T_{hot} \sim 500^{\circ}\text{C}$ with maximum efficiency of >11% with $T_{hot} \sim 500^{\circ}\text{C}$ and $T_{cold} \sim 25^{\circ}\text{C}$. In addition to the single-stage results, two-stage devices consisting of the same n-PbTe and p-TAGS elements combined in a cascade structure with bulk Bi₂Te₃-based devices will be discussed with conversion efficiencies >13% verified with the Q-meter test apparatus. We will also report on early integration with Bi₂Te₃-based thin-film superlattice devices as the bottom stage of the two-stage device. These devices are being developed to convert waste heat present in the exhaust of portable diesel generators for the Army under a SERDP (Strategic Environmental Research and Development Program) funded

effort. D-STAR engineering has characterized a 3kW generator and shown that temperatures up to $\sim 470^{\circ}\text{C}$ are present in the exhaust. With this information and D-STAR's heat exchanger design, we are attempting to develop a two-stage thermoelectric converter to enable 10% fuel efficiency gain over normal operation. The engineers at U.S. Army CERDEC are helping in the evaluation of the converter system and the testing of the power generation unit. Early studies of this integration with heat-exchanger and system-level tests will be presented. Acknowledgements: SERDP Contract No: W912HQ-08-C-0013

10:30 AM ***N1.4**

Thermoelectric Generators Made with Novel Lead Telluride Based Materials. Timothy Paul Hogan¹, Chun I Wu¹, Jonathan J D'Angelo¹, Nuraddin Matchanov¹, Muhammad Farhan¹, Muhammad Khan¹, Fei Ren², Brad D Hall², Jennifer E Ni², Eldon D Case², Ed Timm³, Harold J Schock³, Joe Sootsman⁴, Steven Girard⁴ and Mercouri G Kanatzidis⁴; ¹Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan; ²Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan; ³Mechanical Engineering Department, Michigan State University, East Lansing, Michigan; ⁴Chemistry Department, Northwestern University, Evanston, Illinois.

Thermoelectric modules made from novel lead telluride based materials have been fabricated and tested. Open circuit voltages measured on modules of $\text{Ag}_1\text{-xPbmSbTe}_{2+\text{m}}$ (n-type) legs and $\text{Ag}(\text{PbSn})\text{mSbTe}_{2+\text{m}}$ (p-type) legs have shown good agreement with expected values based on temperature dependent material properties. Systematic improvements in the parasitic electrical losses have resulted in increased short circuit electrical current output from these modules to over 5.5 (A) for a hot side temperature of 870K, and a cold side of 300K. Modules based on segmented legs using $\text{Bi}_2\text{Te}_3\text{-xSex}$ and $\text{BiSb}_2\text{-xTe}_3$ materials for the colder sides will also be presented. Common thermoelectrics are narrow bandgap semiconductors which are brittle, and mechanical characterization of these materials is essential for the design of robust modules. Through powder processing and hot pressing techniques, the fracture strength of these materials has been increased by as much as a factor of 3. Investigations of contacts for reducing the electrical parasitic resistances will be presented along with the latest advancements in the fabrication and characteristics of modules based on these and other novel high ZT materials developed in our group.

11:00 AM **N1.5**

Fabrication of Power Generating Couples Using Advanced Thermoelectric Materials. Erik J. Brandon¹, Thierry Caillat¹, Su Chi¹, Richard Ewell¹, Samad Firdosy¹, Billy Li¹, Bill Nesmith¹, Jong-Ah Paik¹ and Vilupanur Ravi^{1,2}; ¹Materials and Device Technologies Group, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California; ²Department of Chemical and Materials Engineering, California State Polytechnic University, Pomona, California.

A next generation thermoelectric power converter for use in deep space missions is currently under development. This development effort is driven by increasingly ambitious science goals for future NASA robotic missions, combined with a decreasing availability of plutonium fuel. The goal of this current effort is to demonstrate improved system specific power and efficiency relative to the General Purpose Heat Source Radioisotope Thermoelectric Generator (GPHS-RTG) used in previous missions (such as Galileo, Ulysses, Cassini and New Horizons to Pluto) as well as the Multi-mission Radioisotope Thermoelectric Generator (MMRTG) planned for use in upcoming missions. The specific system performance goals are an 8-10% thermal-to-electric conversion efficiency and a 6-8 W/kg specific power. The key to meeting these system performance goals is the planned use of power generating thermocouples incorporating advanced thermoelectric materials that are capable of operating with a maximum zT near a hot side temperature of 1000°C for up to 14 years of service. Several promising p-type and n-type semiconductor materials are currently under development, for incorporation into thermocouples. One candidate p-type material under investigation is the compound $\text{Yb}_{14}\text{MnSb}_{11}$, which exhibits a Zintl structure type and electrical properties on the borderline between a semiconductor and a metal. Although $\text{Yb}_{14}\text{MnSb}_{11}$ has a favorable zT of >1 near 1000°C , this compound exhibits a high sublimation rate and a pronounced tendency to form oxides. The lack of a well defined phase diagram for this ternary compound combined with the limited availability of reactivity data make the design of appropriate bonding technologies challenging. Furthermore, its coefficient of thermal expansion is high relative to widely used n-type materials such as silicon germanium alloys, making their joining to a common hot side member difficult. To enable the incorporation of $\text{Yb}_{14}\text{MnSb}_{11}$ into thermocouples requires a better understanding of its reactivity combined with unique approaches to the thermocouple design and fabrication process. In addition, new nano-structured p-type and n-type silicon germanium alloys are currently under development, exhibiting lower thermal conductivities, simpler synthetic routes and more homogenous compositions than previous materials. The challenges of integrating these new materials into power generating thermocouples will be reviewed in this talk.

11:15 AM **N1.6**

Short Time Transient Behavior of SiGe-based Microrefrigerators. Ezzahri Younes, James Christofferson, Kerry Maize and Ali Shakouri; Electrical Engineering, UCSC, Santa Cruz, California.

We use Thermoreflectance Thermal Imaging technique to study the transient cooling of SiGe-based microrefrigerators. Thermal imaging with submicron spatial resolution, 0.1C temperature resolution and 300 nanosecond temporal resolution is achieved. Transient temperature profiles of SiGe-based superlattice microrefrigerator devices of different sizes are obtained. The dynamic behavior of these microrefrigerators, show an interplay between Peltier and Joule effects. Peltier cooling appears first with a time constant of about 10-20 microseconds, then Joule heating in the device starts taking over with a time constant of about 100-150 microseconds. The experimental results agree very well with the theoretical predictions based on Thermal Quadrupoles Method. The difference in the two time constants can be explained considering the thermal resistance and capacitance of the thin film. In addition this shows that the Joule heating at the top metal/semiconductor interface does not dominate the microrefrigerator performance. If this was the case, we would have obtained the same time constants for Peltier and Joule effects. Experimental results show that under high current values, pulse-operation the microrefrigerator device can provide cooling for about 30

microseconds, even though steady state measurements show heating. Temperature distribution on the metal leads connected to the microrefrigerator's cold junction show the interplay between Joule heating in the metal as well as heat conduction to the substrate. Modeling is used to study the effect of different physical and geometrical parameters of the device on its transient cooling. 3D geometry of heat and current flow in the device plays an important role. One of the goals is to maximize cooling over the shortest time scales.

11:30 AM N1.7

Materials for Solar Thermoelectric Generators. Reja Amaty and Rajeev J Ram; EECS, MIT, Cambridge, Massachusetts.

Solar thermoelectric generators employing light concentrators and high ZT thermoelectric materials are an attractive alternative to solar photovoltaics for micro-power applications. We have shown that cost savings of 30% can be realized over comparable photovoltaic technology. In this paper we report on optimization of thermoelectric materials for this important energy application. Specifically, we present a new thermodynamic analysis of solar thermoelectrics that is experimentally verified for a subset of materials. Solar TE generator performance is modeled and measured using mature thermoelectric materials (micro-alloy Bi₂Te₃ & SiGe) as well as novel nanocomposite materials ([PbTe, ErAs:InGaAs]). In addition, we explore the optimal choice of material for this application. Solar TE requires: 1. a fixed input power density with low-cost light concentrators providing 10,000 W/m², 2. a high optimal temperature (set in-part by thermodynamic balance between concentrator and TE hot-side) of 800-900 C, and 3. a wide-operating temperature over various hours in the day and seasons in the year. For example, a TE element with a thermal conductivity of 4.13 W/m/K and an aspect ratio (cross-section area/length) of 0.01m, with a cold-side heat transfer coefficient of 1.5 W/cm²/K gives a hot-side temperature of 1200K. A ZT = 0.45 at the absorber temperature of 1200K gives the system efficiency of 3.8%.

11:45 AM N1.8

High Power Density Thermoelectric Modules for Thermal Energy Harvesting John B. Posthill¹ and Jerry Fleming²; ¹Center for Solid State Energetics, RTI International, Research Triangle Park, North Carolina; ²Secure Computing and Communications Group, Luna Innovations Incorporated, Roanoke, Virginia.

The potential for energy harvesting from waste heat is becoming an increasingly important topic for both military and commercial systems. The integration of thermoelectric devices to perform this task can be challenging and must compete for space and area with other important functionality in the system. Ideally, incorporating a new capability (such as energy harvesting) into a material or structure with little-to-no adverse impact on other properties is desired. This has led to the concept and study of multifunctional materials. We have conducted an initial investigation and comparison between commercial, bulk Bi₂Te₃-based Peltier thermoelectric devices with thin-film Bi₂Te₃-based thermoelectric modules. The metrics we have used for this comparison are: (1) power density based on area (PD_a in units of mW/cm²) and (2) power density based on volume (PD_v in units of W/cm³). Power results were obtained as a function of externally applied temperature difference (ΔT) in the range from 5K to 150K, with the subsequent power densities calculated from the area of the hot side header and the module thickness. The point of comparison between modules was chosen to be $\Delta T = 25K$. The thin film modules with a packing fraction 18.1% and appropriately thinned headers demonstrated PD_a = 184 mW/cm² and PD_v = 2.84 W/cm³ at $\Delta T = 25K$. As ΔT was raised to 150K, PD_a = 6,530 mW/cm² and PD_v = 100 W/cm³ were measured, thereby demonstrating the expected ΔT^2 dependency. We are unaware of higher power density results than these from a single-stage Bi₂Te₃-based thermoelectric module. Comparative results varied because a number of commercial thermoelectric modules were tested, though smaller commercial modules of area 1cm² or less were chosen. Packing fractions as well as the module heights varied based (presumably) on commercial considerations, not necessarily on maximizing power density. Nevertheless, we found at a $\Delta T = 25K$ for the smallest bulk module chosen, the thin film module exceeded commercial bulk modules by a factor of 6.8 for PD_a and by a factor of 21.8 for PD_v. These results will also be compared with other thin film thermoelectric results in the literature. Direction for future increases in thermal energy harvesting power density will be discussed as well as comparative thermoelectric module efficiency as a function of ΔT .

SESSION N2: Nanocomposites and Nanostructured Materials I

Chairs: Joseph Heremans and George Nolas

Tuesday Afternoon, April 14, 2009

Room 2010 (Moscone West)

1:30 PM *N2.1

The Promise of Nanocomposite Thermoelectric Materials. Mildred S. Dresselhaus¹, Gang Chen², Zhifeng Ren³ and Jean-Pierre Fleurbaey⁴; ¹Electrical Engineering and Computer Science and Physics, MIT, Cambridge, Massachusetts; ²Department of Mechanical Engineering, MIT, Cambridge, Massachusetts; ³Department of Physics, Boston College, Chestnut Hill, Massachusetts; ⁴Jet Propulsion Laboratory, Pasadena, California.

The concept of using nanocomposite thermoelectric materials in bulk form for practical applications is presented. Laboratory studies have shown the possibilities of nanostructures to yield large reductions in the thermal conductivity while at the same time increasing the power factor, and theoretical studies have suggested that structural ordering in nanosystems is not necessary for the enhancement of ZT, leading to the idea of using nanocomposites as a practical scale-up technology for making bulk thermoelectric materials with enhanced ZT values. Specific examples of nanocomposite thermoelectric materials developed by

our group based on the familiar bismuth telluride and silicon germanium systems showing enhanced thermoelectric performance through nano-structuring are presented.

2:00 PM *N2.2

Optimizing Electronic Properties of Misfit Layered Compounds. Qiyin Lin, Clay Mortensen, Colby Heideman, Ngoc Nguyen, Raimar Rostek, Mary Smeller and David C. Johnson; Materials Science Institute and Department of Chemistry, University of Oregon, Eugene, Oregon.

Misfit layered compounds are naturally occurring nanostructured solids that have been reported to have power factors as large as 10^{-3} Wm⁻¹K⁻², low thermal conductivities on the order of 0.8 Wm⁻¹K⁻¹, and unoptimized figures of merit ZT as large as 0.3. We have recently reported thermal conductivity in [(PbSe)_{1.00}][MoSe₂]_n and [(PbSe)_{0.99}][WSe₂]_n misfit compounds as low as 0.06 Wm⁻¹K⁻¹. Here we describe annealing treatments of these misfit compounds in fixed chalcogen partial vapour pressures and demonstrate that samples equilibrate with the dominant source of vapour, resulting in controlled carrier concentrations. The thermal stability of these materials allows annealing times and temperatures in excess of 24 hours and 500° C to be used without destroying the layered structure. Holding the sample at constant temperature while changing the reservoir's annealing temperature provides an independent means to control chalcogen partial pressure and hence carrier concentrations. We present data showing the convergence of electrical properties for isostructural samples on annealing. In addition to control of carrier concentrations, the annealing treatments dramatically improve the carrier mobility. We report electrical resistivity, Seebeck coefficients and carrier concentrations as a function of annealing conditions.

2:30 PM N2.3

The "Nanoparticle in Alloy" Approach to Efficient Thermoelectrics: Silicides in SiGe. Natalio Mingo^{1,2}, David Hauser¹, Nobuhiko Kobayashi², Marc Plissonnier¹ and Ali Shakouri²; ¹LITEN, CEA-Grenoble, Grenoble, France; ²Jack Baskin School of Engineering, University of California at Santa Cruz, Santa Cruz, California.

We present a "nanoparticle-in-alloy" material approach, with silicide and germanide fillers, leading to a potential five fold increase in the thermoelectric figure of merit of SiGe alloys at room temperature, and 2.5 times increase at 900K. Strong reductions in computed thermal conductivity are obtained for 17 different types of silicide nanoparticles. We predict the existence of an optimal nanoparticle size that minimizes the nanocomposite's thermal conductivity. This thermal conductivity reduction is much stronger, and strikingly less sensitive to nanoparticle size, for an alloy matrix than for a single crystal one. At the same time, nanoparticles do not negatively affect the electronic conduction properties of the alloy. The proposed material can be monolithically integrated into Si technology, enabling an unprecedented potential for micro refrigeration on a chip. High figure-of-merit at high temperatures (ZT~1.7 at 900K) opens up new opportunities for thermoelectric power generation and waste heat recovery at large scale.

2:45 PM N2.4

High Temperature Thermoelectric Properties of Nano-Bulk Silicon. Jean-Pierre Fleurial¹, Sabah Bux^{1,2}, Richard Blair³, Pawan Gogna¹ and Richard Kaner²; ¹Power and Sensor Systems Group, Jet Propulsion Laboratory/California Institute of Technology, Pasadena, California; ²Chemistry and California NanoSystems Institute, University of California, Los Angeles, Los Angeles, California; ³Chemistry, University of Central Florida, Orlando, Florida.

Point defect scattering via the formation of solid solutions has been an effective method of increasing ZT in state-of-the-art materials such as Bi₂Te₃-Sb₂Te₃ and PbTe-SnTe by reducing the lattice thermal conductivity. However, increases in ZT are limited by a concurrent decrease in charge carrier mobility values. The search for effective methods for decoupling electronic and thermal transport led to the study of low dimensional thin film and wire structures, in particular because scattering rates for phonons and electrons can be controlled independently. While promising results have been achieved on several material systems, integration of low dimensional structures into practical power generation devices that need to operate across a large temperature differential is extremely challenging. We present achieving similar effects on the bulk scale via high pressure sintering of doped and undoped Si. The nanoparticles are prepared via techniques that include high energy ball milling of the pure elements. The nanostructure of the materials is confirmed by powder X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and dynamic light scattering. Thermal conductivity measurements on the densified pellets show a drastic 90% reduction in the lattice contribution at room temperature when compared to doped single crystal Si. Additionally, Hall Effect measurements show a much more limited degradation in the carrier mobility. The combination of low thermal conductivity and high power factor in heavily doped n-type nanostructured bulk Si leads to an unprecedented increase in ZT at 1275 K by a factor of 3.5 over that of single crystalline samples. Experimental results on both n-type and p-type Si are discussed in terms of the impact of the size distribution of the nanoparticles, doping impurities and nanoparticle synthesis processes.

3:30 PM *N2.5

Nanostructured PbTe-based Thermoelectrics for Power Generation. Mercouri G. Kanatzidis, Department of Chemistry, Northwestern University, Evanston, Illinois; Materials Science Division, Argonne National Laboratory, Argonne, Illinois.

There is a strong incentive to develop highly efficient thermoelectric materials for power generation. Recently, we have reported a number of novel PbTe-based materials with substantially enhanced figures of merit including AgPb₁₈+xSbTe₂₀ (LAST-18), NaPb₂₀+xSbTe₂₂ (SALT-20), AgPb₁₈-nSnnSbTe₂₀ (LASTT), PbTe-Sb-Pb, PbTe-PbS. All these systems are characterized by a strong tendency to nano-segregate into well defined nanostructured entities. The mechanism of nanostructuring results in coherent and semi-coherent nanometer sized inclusions in a PbTe matrix. The inclusions can serve as sites for scattering of

acoustic phonons thereby lowering the lattice thermal conductivity. It is now realized that the fundamental length scales involved in this type of energy conversion processes fall in the nanoscale regime. Fundamental scientific information regarding the influence of nanostructures on TE properties is mounting. However new phenomena are being discovered. For example, in the case of co-nanostructuring PbTe with nanoparticles of Pb and Sb results in unexpectedly electron high mobilities at high temperature and in large enhancements in power factor. The mechanism for this enhancement is not well understood. The talk will end with some vision as to where we think the field of thermoelectrics is now going.

4:00 PM N2.6

Precipitation of Silver Telluride in Rocksalt-Structured Thermoelectric Materials Douglas L. Medlin¹, J. D. Sugar¹, P. A. Sharma¹, M. Hekmaty¹ and T. Drye^{1,2}; ¹Materials Physics Department, Sandia National Labs, Livermore, California; ²Department of Physics and Astronomy, Clemson University, Clemson, South Carolina.

An emerging approach to improving the performance of bulk thermoelectric materials is to introduce nanoscale distributions of embedded interfaces through solid-state precipitation. Understanding the phase stability and microstructural evolution within such bulk thermoelectric materials is a key to designing materials processing approaches for optimal performance and to predicting the long-term stability of the material. In this presentation, we discuss the formation of nanoscale precipitates of silver telluride (Ag_2Te) in rock-salt structured thermoelectric materials. We focus on the Ag_2Te -PbTe system. PbTe is a rocksalt-structured material, while Ag_2Te undergoes a transformation at 145°C from a high temperature cubic structure to a low-temperature monoclinic phase. By controlling the composition and thermal history in alloys of Ag_2Te -PbTe, we are able to produce a fine distribution of nanoscale Ag_2Te precipitates in a PbTe matrix. We analyze this microstructure using a combination of transmission electron microscopy and atom probe tomography. The reduction in symmetry of the Ag_2Te phase in transforming from the high temperature cubic structure to the low temperature monoclinic structure produces a complex set of orientation variants. By establishing the details of these orientation relationships, we show how the Ag_2Te forms through the topotactic alignment of the Te sublattices in the two phases. Finally, we relate these observations to the precipitation of Ag_2Te in the closely related rocksalt structured compounds of the LAST system $((\text{AgSbTe}_2)_{1-x}(\text{PbTe})_x)$ and in AgSbTe_2 .

4:15 PM N2.7

Investigation of Solid-State Immiscibility and Thermoelectric Properties of the System PbTe - SnTe - PbS. Steven N. Girard¹, Jiaqing He², Vinayak P. Dravid² and Mercouri G. Kanatzidis¹; ¹Chemistry, Northwestern University, Evanston, Illinois; ²Materials Science and Engineering, Northwestern University, Evanston, Illinois.

Well-documented solid-state immiscibility in the material $\text{PbS}_x\text{Te}_{1-x}$ has been shown to produce distinct nanostructures that will vary in size and morphology depending on thermal treatment and composition. Toward the middle of the composition range, phase segregation occurs through spinodal decomposition, characterized by small compositional fluctuations that extend over large areas. Toward the outer extremes of the composition range, phase segregation occurs through nucleation and growth, characterized by large compositional differences that are small in scale. Conversely, $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ has been implemented as a useful thermoelectric alloy exhibiting solid solution behavior. For the material $(\text{Pb}_{0.95}\text{Sn}_{0.05}\text{Te})_{1-x}(\text{PbS})_x$ ($x = 0.04, 0.08, 0.16, 0.30$) nanostructuring from nucleation and growth and spinodal decomposition has been shown to enhance the thermoelectric figure of merit over bulk PbTe, producing ZT 1.1 - 1.4 at 650 K for $x = 0.08$. However, the influence of varying Sn substitution for Pb has not yet been addressed. In this work, we show that for small amounts of Sn substitution for Pb (<5%), the solubility of PbS is increased within the host material, while increased Sn substitution (>5%) results in massive phase segregation of the minor phases. Detailed microscopy analysis will be presented to describe observed phase separation phenomena in conjunction with electrical conductivity, Seebeck coefficient, thermal conductivity, and Hall effect measurements.

4:30 PM N2.8

Enhanced Thermoelectric Performance in Bi_{0.52}Sb_{1.48}Te₃ Alloy with Novel Nanostructures. Wenjie Xie^{1,2}, Xinfeng Tang¹, Yonggao Yan¹, Qingjie Zhang¹ and Terry M. Tritt^{1,2}; ¹State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei, China; ²Department of Physics & Astronomy, Clemson University, Clemson, South Carolina.

We report a novel melt-spin (MS) technique followed by spark plasma sintering procedure to obtain high performance p-type Bi_{0.52}Sb_{1.48}Te₃ bulk material. The microscopy study revealed novel nanoscale microstructures, which features an amorphous phase and a large number of 10 nm-scale nanocrystals with coherent interfaces. It is found that the MS technique induced nanostructure yields an optimized transport of phonons and electrons, resulting in a maximum figure of merit ZT value of 1.56 at 300 K for p-type Bi_{0.52}Sb_{1.48}Te₃ bulk material. The ZT value is over a 50% improvement of that of the state of the art commercial Bi₂Te₃ materials. In addition, all samples showed good thermal stability in the temperature range of 300-400 K. The present work offers a new route for developing high performance bismuth telluride based alloys and devices, which have even broader prospects for commercial applications.

4:45 PM N2.9

Thermoelectric Properties of Solution-Processed Bismuth Chalcogenides. Robert Yue-Sheng Wang^{1,2}, Joseph P. Feser²,

Antje G Rey³, Delia Milliron¹, Jeffrey J Urban¹, Rachel A Segalman^{1,2} and Arun Majumdar^{1,2}; ¹Lawrence Berkeley National Laboratory, Berkeley, California; ²University of California, Berkeley, Berkeley, California; ³ETH Zürich, Zürich, Switzerland.

The benefits of solution-processable thermoelectric materials are extremely attractive. Such a development could lead to the widespread use of low-cost thermoelectric coolers and power generators. I present work on our development of soluble precursors for bismuth chalcogenide materials. In particular, we have created a soluble bismuth sulfide precursor by mixing bismuth sulfide with sulfur and hydrazine. This soluble precursor can be spin-coated, printed, and/or stamped and then converted back into polycrystalline bismuth sulfide by thermal decomposition. Our results suggest that precursor-based bismuth sulfide has a thermopower and electrical conductivity of approximately - 200 $\mu\text{V/K}$ and 0.1 S/cm, respectively. We anticipate that further development of this material will lead to improved properties. For instance, this material could be alloyed and doped by mixing precursors for bismuth sulfide and antimony sulfide to create bismuth antimony sulfide. The sulfur content in this material, which is adjusted by varying the thermal decomposition parameters, can also be used to tune carrier concentration. We also have ongoing efforts to develop soluble precursors for other bismuth chalcogenide materials such as bismuth selenide and bismuth telluride. Lastly, we anticipate creating solution-processable nanocomposites using this precursor chemistry. For instance, this chemistry can be used to embed nanoparticles inside a matrix material. This is done by dispersing nanoparticles inside the precursor solution and then decomposing the precursor. This nanocomposite is thematically similar to other successful nanostructured thermoelectric materials, but also benefits from a simple wet chemistry synthesis.

SESSION N3: Poster Session: Materials and Devices for Thermal-to-Electric Energy Conversion
Chairs: Yuri Grin, Kunihito Koumoto, George Nolas and Jihui Yang
Tuesday Evening, April 14, 2009
8:00 PM
Exhibition Hall (Moscone West)

N3.1

Link Between Changes in ZT and Microstructure in AgSbTe_2 . Peter Sharma, Joshua D Sugar and Douglas L Medlin; Materials Physics, Sandia National Laboratories, Livermore, California.

Some high performance thermoelectric alloys have complex microstructures. For example, the LAST alloys, $(\text{AgSbTe}_2)_{1-x}(\text{PbTe})_x$, are one of the best thermoelectrics ($\text{ZT} \sim 1.5-2$) but have a great variety of inclusions with different chemistry at different length scales. How does microstructure affect thermoelectric efficiency? Since the phase diagram of this and most quaternary alloys is poorly known, transport properties have not been systematically connected to microstructure. We are attacking this problem by studying the simple ternary alloy AgSbTe_2 , a component of the LAST system, in order to show how thermoelectric transport changes with a known, controlled microstructure. AgSbTe_2 forms within the well-studied $\text{Ag}_2\text{Te}-\text{Sb}_2\text{Te}_3$ pseudobinary phase diagram. We have found that Sb-rich AgSbTe_2 is composed of Sb_2Te_3 precipitates embedded in a homogeneous rocksalt $\text{Ag}_{16}\text{Sb}_{30}\text{Te}_{54}$ matrix. The precipitates are plate-like and crystallographically aligned along their close packed planes parallel to that of the matrix. The size of these Sb_2Te_3 plates can be tuned from the nanometer to micron scale. In this work, the formation and growth of precipitates over a wide length scale is linked to changes in thermoelectric properties for the first time. This study is useful for understanding the complexity of LAST, or any bulk thermoelectric where second phase precipitation occurs.

N3.2

Nano-Carbon Ensembles: From their Structure to Their Thermoelectric Properties. Raul Arenal^{1,2}, Paola Bruno², Dileep Singh³, Jules Routbort³, Ming Xie^{2,4} and Dieter Gruen²; ¹LEM, CNRS-ONERA, Chatillon, France; ²Materials Science Division, Argonne National Laboratory, Argonne, Illinois; ³NED, Argonne National Laboratory, Argonne, Illinois; ⁴Dept. of Physics, Michigan Technological University, Houghton, Michigan.

In this communication we will present the exceptional thermoelectric properties displayed by nanocarbon ensembles (NCE's) as well as their structural modifications under thermal treatments. These NCE's consist in compact carbon nanostructured materials (1D, 2D and 3D) produced by heating nanographite or nanodiamond powders with or without boron carbide powders in a stream of methane up to 1200 K. Concerning the thermoelectric properties, we observe that the thermopower factor in these samples displays strongly temperature dependent and increases by more than an order of magnitude over undoped/untreated carbon ensembles [1]. The transformation of these materials at different temperatures is followed in detail making use of the high resolution transmission electron microscope (TEM), electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), X-ray diffraction (XRD) measurements as well as Raman spectroscopy. The results from these techniques indicate a clear modification (graphitization) of the original materials with their annealing to 2500 K. During these annealing treatments different kinds of nanocarbon materials are produced and have been observed by TEM: single-wall nanohorns, polyhedral nanostructures, onion-like graphite, fullerenes (isolated), nanotubes, turbostratic and even amorphous/disordered carbon phases. Moreover, in the case of the NCE's fabricated including B4C powders, crumpled sets of few layer graphene as well as boron carbide particles are also present. Thus a close relationship between the structure of the NCE's and their thermoelectric properties has been observed [2] and will be presented in this communication. [1] D.M. Gruen, P. Bruno, M. Xie, Appl. Phys. Lett. 92, 143118 (2008). [2] R. Arenal, P. Bruno, D. Singh, J. Routbort, D.M. Gruen, in preparation. Acknowledgements This work was supported by the U.S. Department of Energy, Office of Science, Contract No. DE-AC02-06CH11357.

N3.3

Microstructure of Multiphase Thermoelectric Ag-Sb-Te Alloys Joshua D. Sugar, Peter A Sharma and Douglas L Medlin; Materials Physics Department, Sandia National Laboratories, Livermore, California.

AgSbTe₂ has only three components, and thus is one of the simplest high ZT (~1.3 at 700 K) thermoelectric compounds. The microstructure of this system, however, is not well understood. In this presentation, two stoichiometries of Ag-Sb-Te alloys are compared, AgSbTe₂ and Ag₁₆Sb₃₀Te₅₄, both of which lie on the pseudobinary Ag₂Te-Sb₂Te₃ phase diagram. AgSbTe₂ phase separates into a two-phase mixture of a rocksalt matrix (Ag₂₂Sb₂₈Te₅₀) and crystallographically aligned, monoclinic Ag₂Te precipitates. The Ag₂Te precipitates can easily form because of the close alignment of the Te sublattices in both phases at elevated temperature. At elevated temperatures (~550°C), Ag₁₆Sb₃₀Te₅₄ is a single-phase rocksalt-structured compound, but at lower temperatures (~500°C), second-phase, tetradymite-structured Sb₂Te₃ can be controllably precipitated. These precipitates form as plates with the close-packed planes and close-packed directions of both phases aligned. The formation of precipitates at various length scales, and details of the interface structure between Ag₁₆Sb₃₀Te₅₄ and Sb₂Te₃ are explained. These results provide insight into engineering nanostructured materials for high ZT.

N3.4

Abstract Withdrawn

N3.5

Thermoelectric Properties of Nb-Doped SrTiO₃ / TiO₂ Multiphase Composite Kiyoshi Fuda¹, Kenji Murakami¹, Tomoyoshi Shoji¹ and Shigeaki Sugiyama²; ¹App. Chem. for Environ., Akita University, Akita, Japan; ²Akita pref. Ind. Tech. Center, Akita, Japan.

In this study, we fabricated and examined a series of multiphase type composites constructed of Nb-doped SrTiO₃ / TiO₂ fine particles. The composites were prepared via two processing steps: (1) precursor oxide preparation by wet processes; (2) sintering by using spark plasma sintering (SPS) apparatus. The composition of the composites and the sintering temperatures were selected in a region where a perovskite SrTiO₃ and a rutile TiO₂ phases coexist in stable. The microscopic structure was examined by using scanning electron microscope (SEM; HITACHI S-4500 model) attached with an energy dispersive x-ray spectroscopy. The electrical conductivities and the Seebeck coefficients were measured simultaneously using an ULVAC ZEM-1 instrument in helium atmosphere. The thermal diffusivities were measured by a laser flash method in vacuum. The composites obtained here were found to commonly have a mosaic type texture constructed of TiO₂ and SrTiO₃ fine particles with a typical size of about 500 nm. In some samples we also found additive phases such as Sr₆Ti₇Nb₉O₄₂. The thermal conductivity values measured for the most samples with different contents are ranged between 2 and 5 Wm⁻¹K⁻¹ in the temperature range from room temperature to 800 C. The values are apparently lower than the value for single crystal SrTiO₃ samples presented in literature. A sample with rather low relative density of about 80% showed a quite low thermal conductivity, about 1 Wm⁻¹K⁻¹. Taking account the other TE data, e.g. Seebeck coefficient and electrical conductivity, we calculated dimensionless figure of merit, ZT, to be at maximum 0.24 at 600°C.

N3.6

Raman Scattering Characterization for Crystalline Quality of Doped n-type Mg₂Si Prepared by Melt Growth and Plasma Activated Sintering Techniques. Daisuke Mori¹, Tsutomu Iida¹, Masayasu Akasaka², Takashi Nemoto³, Makoto Ogi¹, Keishi Nishio¹ and Yoshifumi Takanashi¹; ¹Tokyo University of Science, Noda-shi, Japan; ²Dow Corning Toray Co., Ltd., Ichihara-shi, Japan; ³Nippon Thermostat Co., Ltd., Kiyose-shi, Japan.

Mg₂Si, an environmentally benign semiconductor, is a promising thermoelectric material at temperatures ranging from 500 to 800 K. Although Mg₂Si is the only stoichiometric silicide in the Mg-Si phase diagram, the conditions for high-quality crystals and the doping control are not well-established yet. This is mainly due to a high reactivity of molten and/or vapor Mg at an elevated growth temperature, while Bi-doped n-type Mg₂Si exhibited ZT=1.08 at ~800 K as tentative results. In order to realize the commercial method for a large quantity of Mg₂Si synthesis, a plasma activated sintering method seems to provide better throughput than the melt-growth method, while residual source materials of Mg and Si which are attributed to plasma sintering process degrade thermoelectric (TE) performance of Mg₂Si easily. However, it has been reported that the use of an all melted synthetic Mg₂Si source by UNION MATERIAL provides higher performance and longer lifetime at elevated operation temperature as compared with former Mg₂Si TE devices. In this article, we report following examination of (i) the solution growth of the Mg₂Si by means of a conventional vertical Bridgman method, (ii) sintering synthesis with plasma activated sintering (PAS) method, (iii) systematic n-type impurity (Bi, Al) doping into Mg₂Si, and (iv) test electrode formation. For entire experiments, all melted synthetic Mg₂Si source provided by UNION MATERIAL was used. The fabricated specimens were characterized using Raman scattering measurements in a backscattering geometry, to understand the crystalline quality and lattice deformation which is brought about by the substitution of larger or smaller dopant atoms for host atoms and by incorporation interstitially. The grown crystals were multicrystalline with large grains and showed n-type conductivity in undoped condition. In grown samples, a single peak at 253 cm⁻¹ was observed, which is assigned as the dominant phonon signals of Mg₂Si. The Raman signal appeared in PAS samples at 253 cm⁻¹ indicate that Mg₂Si prepared by PAS showed sufficient lattice quality even in the as-sintered condition. For doped specimens, dominant phonon signal shifted higher or lower frequencies depending on the doping concentration of Bi or Al with slight decrease in signal intensity. From the observed frequency shift of this dominant phonon signal, the local stress involved in the fabricated specimens can be determined indicating compressive or tensile stress as a function of the synthesis methods, dopant incorporation. At the interface between Mg₂Si and electrode materials such as Ni, Cu and TiN, results of precise Raman

measurement will be demonstrated to understand the local stress due to the different thermal expansion coefficient.

N3.7

Morphologies and Characteristics of Bi₂Te₃ Nano-wires and Tubes Prepared by Solvothermal & Hydrothermal Synthesis. Hee Jin Kim¹, Ha-yeong Kim¹, SeungHyun Lee², Wooyoung Lee² and Sung-Jin Kim¹; ¹Department of Chemistry, Nano Science, Ewha Womans University, Seoul, Korea, South; ²Department of Metallurgical Engineering, Yonsei University, Seoul, Korea, South.

The thermoelectric devices of conversion heat to electricity may be significant in the near future for energy production. The thermoelectric device ability is measured by figure of merit ZT, where ZT is given by $ZT = S^2\sigma T / \kappa$ (where σ is the electrical conductivity, S the thermo power, and κ is the thermal conductivity). For several decades, the ZT of the thermoelectric materials have had less than 1. Current research results often are reported $ZT > 2$ due to quantum confinement effect. Bismuth telluride, Bi₂Te₃ is the most important thermoelectric materials used in the devices for the various temperature ranges due to low thermal conductivity. Many researcher have been studied to improve ZT value by making the nano-structured Bi₂Te₃ material [1,2], Bi₂Te₃ super-lattice thin films[3,4,5], Bi₂Te₃ nano-wires prepared by electrochemical deposition[6] and the solvothermal synthesized Bi₂Te₃ nano-tubes[7]. However, measuring ZT value of nano structured materials such as nano-wire, rod and tubes has been challenging tasks. Bi₂Te₃ nano-wires and tubes were prepared by solvothermal and hydrothermal synthesis, respectively, and there thermoelectric properties are measured. The microstructure morphology of the bismuth telluride nano-wires and tubes were investigated by Powder X-ray diffraction(Rigaku D/MAX X-ray diffractometer and operating at 40 kV and 30 A) and HR-TEM(High Resolution Transmission electron microscopy, JEOL 2100F). Bismuth telluride nano-wires and tubes were verified a single rhombohedral phase of Bi₂Te₃ (space group of m3R) by XRD and had the sizes of 10-40 nm in diameters and above 5-10 μ m in lengths. The ZT value of hydrothermally and solvothermally synthesized Bi₂Te₃ nano-tubes will be reported. 1. Sander, M. S. et al, "Fabrication of high-density, high aspect ratio, large-area bismuth telluride nanowire arrays by electrodeposition into porous anode alumina templates," Adv. Mater., Vol. 14, No. 9 (2002), pp. 665-667. 2. Martin-González, M. et al, "High-density 40 nm diameter Sb-rich Bi₂-xSb_xTe₃ nanowire arrays," Adv. Mater., Vol. 15, No.12 (2003), pp.1003-1006. 3. Venkatasubramanian, R. E. et al, "Thin-film thermoelectric devices with high room-temperature figures of merit," Nature, Vol. 413 (2001), pp.597-602. 4. Harman, T. C et al, "Quantum dot superlattice thermoelectric materials and devices," Science, Vol. 297 (2002), pp. 2229-2232. 5. Venkatasubramanian, R. E. et al, "Thin-film thermoelectric devices with high room-temperature figures of merit," Nature, Vol. 413 (2001), pp.597-602. 6. Prieto, A. L. et al, "Electrodeposition of Ordered Bi₂Te₃ Nanowires: Arrays," J. Am. Chem. Soc., Vol. 123 (2001), pp. 7160-7161. 7. Deng, Y. et al. "Solvothermal preparation and characterization of nanocrystalline Bi₂Te₃ powder with different morphology," J. Phys. Chem. Solids, Vol. 63 (2002), pp. 2119-2121.

N3.8

Growth of Nanoparticle Coatings of Ca₃Co₄O₉ by a Microwave Plasma Process. Ted Wangensteen, Marek Merlak, Prithish Mukherjee and Sarath Witanachchi; Department of Physics, University of South Florida, Tampa, Florida.

The p-type layered cobaltate compound Ca₃Co₄O₉ offers excellent thermoelectric properties and stability in air up to very high temperatures. Seebeck coefficients as high as -125 μ V/K have been reported for films grown by laser ablation or chemical solution deposition. Since the distortion of the CoO₆ octahedra is known to alter the Fermi energy, low dimensional structures such as thin films provides another avenue to enhance thermoelectric properties. In addition to structural modifications, nanoparticle coatings of this material have the potential to increase phonon scattering at the multiple boundaries to further enhance thermoelectric properties. In this work we report the development of a near-atmospheric pressure microwave plasma process to deposit stoichiometric nanoparticle coatings of Ca₃Co₄O₉. In this method a dilute stoichiometric mixture of Co-acetate and Ca-acetate dissolved in propionic acid is atomized using an ultrasonic nebulizer and injected into a high temperature zone of oxygen plasma. As the aerosol with average diameter of 1.5 μ m flows through the reactor, the solvent is evaporated and the salt is condensed into a nanoparticle. Particles are subjected to sintering during their transit through the plasma which helps to forms the structure and deposits on a substrate. Concentration of the starting solution determines the particle size. Effect of particle size on the transport properties will be presented.

N3.9

Microstructure and Thermoelectric Properties of HfN/ScN Metal/Semiconductor Superlattices for Thermionic Energy Conversion. Polina V Burmistrova^{1,3}, Jeremy L Schroeder^{2,3}, Robert Wortman^{1,3} and Timothy D Sands^{1,2,3}; ¹School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana; ²School of Materials Engineering, Purdue University, West Lafayette, Indiana; ³Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana.

Low-dimensional materials such as superlattices have attracted wide attention for applications in solid-state refrigeration and power generation due to the potential for quantum size and interface effects to enhance thermoelectric properties. Experimental evidence, however, indicates that improvement in the thermoelectric figure-of-merit (ZT) is achieved mainly through reduction of thermal conductivity caused by phonon scattering at interfaces. Several superlattice systems composed of materials with good thermoelectric properties, such as Bi₂Te₃/Sb₂Te₃, PbTe/PbSe, and Si/Ge, have been explored with ZT values above 1 being demonstrated [1]. The thermionic carrier transport in metal/semiconductor superlattices is another promising energy conversion approach based on nanocomposite materials [2]. Despite the poor thermoelectric properties of the individual metal and semiconductor layers, metal/semiconductor superlattices are expected to enhance the power factor ($S^2\sigma$) through energy barrier filtering while suppressing thermal conductivity via interface scattering of phonons. Two nitride solid-state thermionic systems, TiN/GaN and ZrN/ScN, have been previously reported [3],[4]. ZrN/ScN superlattices yielded a Schottky barrier height of 280 meV,

a value that modeling suggests may yield ZT values exceeding 2.5 at temperatures above 650°C. In addition, the minimum thermal conductivity of ZrN/ScN multilayers can be reduced from 5 W/m-K to 1.8 W/m-K by alloying ZrN with W-N. In the present work, the related HfN/ScN superlattice system has been explored in order to further reduce the lattice thermal conductivity. HfN/ScN superlattices of varying periods were deposited on MgO, silicon, and sapphire substrates by reactive DC magnetron sputtering in a high vacuum deposition system with a base pressure of 10^{-8} Torr. First, a 200nm HfN buffer layer was deposited to accommodate lattice strain due to lattice mismatch between the substrate and HfN. Then, HfN/ScN superlattices were sputtered from Hf and Sc targets at 200 W power in an Ar(4sccm)/N₂(6sccm) ambient at 5 mTorr with a substrate temperature of 850°C. The resulting film orientation, texture, and microstructure were characterized by high resolution x-ray diffraction (HRXRD), field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). Superlattices on all three substrates showed <100> texture, with epitaxial relationships in the case of sapphire and MgO. The correlation between thermoelectric and structural properties of HfN/ScN superlattices as a function of substrate material and superlattice period will be discussed in detail. This work was supported by the DARPA Nanostructured Materials for Power program through a grant to UC Santa Cruz. [1] H. Bottner et al., MRS Bulletin 31, (2006). [2] D. Vashaee et al., Phys. Rev. Lett. 92, (2004). [3] V. Rawat et al., J. Appl. Phys. 100, (2006). [4] V. Rawat et al. (under review).

N3.10

Solution Processable Routes to Nanostructured Thermoelectric Devices. Joseph Patrick Feser¹, Robert Wang¹, Jong-Soo Lee³, Dmitri Talapin³, Arun Majumdar¹ and Jeff Urban²; ¹Mechanical Engineering, Univ. of California, Berkeley, Berkeley, California; ²Lawrence-Berkeley National Laboratory, Molecular Foundry, Berkeley, California; ³Chemistry, Univ. of Chicago, Chicago, Illinois.

In the last decade, significant progress has been made in the field of thermoelectrics by exploiting nanostructured semiconductors to a) manipulate the electronic structure of materials and b) reduce lattice thermal conductivity. Despite having achieved ZT values exceeding 2, these materials have not displaced traditional bulk thermoelements, because their synthesis routes are not amenable to production of thick films (>10 μ m's). In the present work, we show that colloiddally grown PbSe nanocrystal's can be formed into superlattices which have a thermopower which is diameter dependent and exceeds those of bulk PbSe. We also show that hydrazine can be used to form soluble precursors of several metal chalcogenide semiconductors which are relevant to thermoelectric devices. We present our ongoing work to characterize the encapsulation of colloidal nanocrystals by matrix materials formed from such soluble precursors.

N3.11

PbTe-Sb₂Te₃ Nanocomposites Prepared by Mechanical Alloying. Chrysi Papageorgiou, Zacharias Viskadourakis, John Giapintzakis and Theodora Kyrtasi; Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus.

Recent research on thermoelectrics focuses on the ability to improve the properties of existing materials with good performance by incorporating nanoscale dimension. PbTe-based materials were found to enhance their thermoelectric performance through this approach. Typical examples are LAST materials where ZT values ranging from 1.5 to 2 at their optimum thermoelectric temperatures have been reported. On the other hand, application of low cost techniques on nano-materials is of the great interest due to the difficulty in applying expensive fabrication processes in commercial systems. Therefore, techniques such as ball milling and sintering are being extensively investigated. In this work PbTe-based nanocomposites are investigated. Nanocrystalline powders of PbTe and Sb₂Te₃ were obtained by mechanical alloying using a high energy planetary ball mill. Mixtures of various concentrations were used to fabricate PbTe-Sb₂Te₃ nanocomposites. The phase of the products was studied by powder X-ray diffraction (PXRD). Thermoelectric measurements were performed on pressed pellets over a wide temperature range from 5 to 300K. The thermal conductivity decreases with increasing Sb₂Te₃ concentration in the PbTe lattice showing significant suppression of the low temperature phonon-drag peak. The Seebeck coefficient and electrical conductivity changes are also discussed.

N3.12

Mechanical Alloying Synthesis of PbTe Nanocrystals: Characterization and Thermoelectric Properties. Chrysi Papageorgiou¹, Euripides Hatzikraniotis², Konstantinos M Paraskevopoulos² and Theodora Kyrtasi¹; ¹Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus; ²Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece.

Nanostructuring is one of the effective approaches to increase the figure-of-merit of thermoelectric materials. Recent work has shown that small, dimensionally-confined systems can exhibit figures of merit well in excess of one. A major trend in recent research involves the incorporation of nanoscale constituents within bulk materials to form nanocomposites. Additionally, application of low cost techniques on the preparation of nano-materials is of great interest; therefore, techniques such as mechanical alloying and sintering are being extensively investigated. In this work, nano-crystalline lead telluride powder was synthesized by mechanical alloying using a high energy planetary ball mill. Phase transformation and crystallite size evolution during ball milling was followed by powder X-ray diffraction (PXRD) and the morphology was studied by scanning electron microscopy (SEM). The broadening of the PXRD peaks vs ball milling time, analyzed by Voigt functions, indicate small crystalline size and introduced stress during mechanical alloying process. Thermoelectric properties and IR spectroscopy results are discussed and compared to the material prepared from melt.

N3.13

Preparation of Delafossite CuYO2 by Metal-citric Acid Complex Decomposition Method. Tomomi Okada¹, Naoto Kikuchi², Satoshi Mikusu³, Tsutomu Iida¹, Kazuyasu Tokiwa³, Tsuneo Watanabe³, Tohru Kineri⁴ and Keishi Nishio¹; ¹Department of Materials Science and Technology, Tokyo University of Science, Noda-shi, Japan; ²Advanced Industrial Science and Technology, Tsukuba, Japan; ³Department of Applied Electronics, Tokyo University of Science, Noda-shi, Japan; ⁴Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, Sanyoonoda-shi, Japan.

Thermoelectric materials having the properties of large thermo-power, low resistivity, and low thermo-conductivity have been investigated. Recently, p-type semiconductor with layered metal oxides, i.e., Na-Co-O and Ca-Co-O, have been reported by many researchers because of their low resistivity and thermo-conductivity. For example, Ca₃Co₄O₉ consists of Ca₂CoO₃ and CoO₂ blocks alternately stacked along the c-axis to form a layered structure. Thus, the physical properties are highly two-dimensional in a-b plane compared with c-axis direction. These layered metal oxide compounds are promising candidate for thermoelectric application at high temperature in air. Recently, CuYO₂ with delafossite structure has been reported as a p-type, wide band-gap semiconductor with high Seebeck coefficient of +275μV. The delafossite also forms a layered structure. Moreover, delafossite materials have a large σ value with low n and high Seebeck coefficient. However, it is needed long time, high temperature heat treatment under low O₂ partial pressure to synthesis delafossite CuYO₂. In this study, we tried to prepare single phase CuYO₂ by the short heating process at lower temperature than ever. The control of carrier concentration of CuYO₂ was also examined by the doping of Ca. The delafossite CuYO₂ and Ca doped CuYO₂ were prepared by thermal decomposition of metal citric acid complex. Cu acetate, Y acetate and Ca acetate used as the raw materials for the starting solution. Citric acid was used as the chelating agent, and acetic acid and distilled water were mixed as a solvent. The starting solutions were heated at 723 K for 5 h after drying at 353 K. The obtained powders were amorphous. Single phase of orthorhombic Cu₂Y₂O₅ was obtained by heating of the amorphous powder at a temperature range between 1073 and 1373K for 3 h in air. The orthorhombic Cu₂Y₂O₅ decomposed to Y₂O₃, CuO and Cu₂O by heat-treated at above 1373K in air. On the other hand, for the sample powder prepared from the starting solution without citric acid, single phase of orthorhombic Cu₂Y₂O₅ could not be obtained in same synthesis condition of that with citric acid. Delafossite CuYO₂ and Ca doped CuYO₂ could be obtained by the heating of orthorhombic Cu₂Y₂O₅ under low O₂ partial pressure at above 1223K. The obtained delafossite CuYO₂ were consisted of hexagonal and rhombohedral phases. The color of the CuYO₂ and Ca doped CuYO₂ powder was light brown and light green, respectively. Diffraction peaks in XRD pattern were slightly shifted by doping of Ca for CuYO₂, and these peaks shifted toward to high diffraction angle with increasing amount of doped Ca. From these results, it is concluded that Ca doped delafossite CuYO₂ could be obtained by thermal decomposition of metal citric acid complex.

N3.14

Long-Term performance of a commercial Thermoelectric Power Generator. Euripides Hatzikraniotis¹, Konstantinos Zorbas¹, Eleni Pavlidou¹, Theodora Kyratsi² and Konstantinos M Paraskevopoulos¹; ¹Physics Dept., Aristotle University of Thessaloniki, Thessaloniki, Greece; ²Department of Mechanical and Manufacturing Engineering, University of Cyprus, Nicosia, Cyprus.

Thermoelectric generators (TEGs) make use of the Seebeck effect in semiconductors for the direct conversion of heat into electrical energy. The possible use of a device consisting of numerous TEG modules in the waste heat recovery can considerably help the world effort for energy savings. However, commercially available TEGs operate at temperatures much lower than the actual operating range in the exhaust pipe of an automobile, and this could cause structural failure of the thermoelectric elements. The exposure of thermoelectric materials to such environments causes, generally, an increase in electrical resistivity, as well as a decrease in material "Figure of merit", Z. Furthermore, the continuous thermal cycling charge, could lead to reduced efficiency and lifetime of the TEG. In this work we investigate the long-term performance and stability of a commercially available TEG under temperature and power cycling. The module was subjected to sequential hot side heating and cooling for 3000 hours, in order to measure the TEG's performance (changes in power and module EMF). Through the development of a theoretical model, which takes into account the contact thermal resistances, we evaluated the changes in resistivity and Seebeck coefficient of the thermoelectric legs. From the results, a reduction of Seebeck coefficient and an increase in resistivity was observed. After the experiment, the module was disassembled and individual legs were examined, regarding their new state with the use of a scanning electron microscope (SEM-EDS) and Fourier transform infrared spectroscopy (FTIR). Results are presented and discussed.

N3.15

Thermoelectric Properties of Bi₂Te₃ Nanowires Synthesized by Lithographically-Patterned Galvanic Displacement Zhaohu Wang¹, Hyunsung Jung², Nosang Myung² and Christopher Dames¹; ¹Mechanical Engr., UC Riverside, Riverside, California; ²CEE, UC Riverside, Riverside, California.

Semiconducting Bi_xTe_y nanowires were prepared using a Lithographically-Patterned Nanowire Galvanic Displacement (LPNGA) method: a new, scalable route to nanostructured thermoelectric materials with the potential for high ZT. The nanowires were synthesized in well-defined locations with controlled composition and dimensions by galvanic displacement of the photolithographically-patterned side-wall of a nickel thin film in acidic nitric electrolyte containing Bi³⁺ and HTeO₂⁺ ions. This approach allows the cross-sectional dimensions of the nanowire to be controlled in the range of several tens of nanometers. The LPNGA method is highly scalable and compatible with current fabrication techniques because it is based on conventional photolithography and galvanic displacement. The electrical conductivity and Seebeck coefficient of LPNGA Bi₂Te₃ nanowires are measured using a hot finger apparatus, which measures the current and voltage response in the presence of a controlled temperature gradient along the nanowire. This apparatus also controls the ambient temperature, allowing temperature-dependent thermoelectric properties to be studied from room temperature to 200 C or above.

N3.16

Syntheses of Ni-doped and Fe-doped CoSb₃ Thermoelectric Nanoparticles through Modified Polyol Process. Takashi Itoh¹ and Keisuke Isogai²; ¹EcoTopia Science Institute, Nagoya University, Nagoya, Japan; ²Department of Materials Science and Engineering, Nagoya University, Nagoya, Japan.

Skutterudite CoSb₃ compounds are of increasing interest as materials with good thermoelectric performance over the temperature range of 600 to 800 K, but the thermal conductivity of the materials is relatively high. Nanostructured materials have been shown to enhance phonon scattering and lower the thermal conductivity of the thermoelectric materials. We have investigated about the synthesis of binary CoSb₃ nanoparticles through a modified polyol process. Partial substitution of Ni or Fe on the Co site of CoSb₃ is a hopeful route for improving thermoelectric performance of the CoSb₃ compounds. In the present work, synthesis of Ni-doped and Fe-doped CoSb₃ nanoparticles through the modified polyol process was attempted and the optimum synthesizing condition was investigated. Co(OOCH₃)₂·4H₂O, Ni(OOCH₃)₂·4H₂O, FeCl₃ and SbCl₃, were prepared as precursors. The precursors were reduced by NaBH₄ in tetraethyleneglycol at 513 K in argon gas, for different reaction time (holding time). The reaction products were characterized by the X-ray diffraction, the energy dispersive X-ray spectroscopy, and transmission electron microscopy. The nanoparticles with about 20 to 30 nm in size mainly existed in the reaction products regardless of the chemical composition and the reaction time. The skutterudite phase was identified as a main phase in the sample synthesized for long reaction time, but the other phases of Sb and MSb₂ (M=Co, Ni, Fe) were also detected. The lattice parameter of the synthesized skutterudite phase linearly increased with increasing the doping agent concentration, following Vegard's law.

N3.17

Output Power Characteristics of Mg₂Si and the Fabrication of a Mg₂Si TE Module with a Unileg Structure. Takashi Nemoto¹, Tutomu Iida², Yohei Oguni², Atsunobu Matsumoto², Junichi Sato¹, Tadao Nakajima¹ and Yoshifumi Takanashi²; ¹Nippon Thermostat Co., LTD., Kiyose-shi Tokyo, Japan; ²Tokyo University of Science, Noda-shi Chiba, Japan.

In order to restrain global warming and to realize a sustainable global energy system, further enhancements in energy efficiency are required. One reliable technology for reducing greenhouse gas emissions and the consumption of fossil fuel is thermoelectric technology, which can directly convert heat into electricity and consequently increases the energy conversion efficiency of power generation by combustion. Magnesium silicide (Mg₂Si) is a promising candidate for a thermal-to-electric energy-conversion material at operating temperatures ranging from 500 to 800 K. Mg₂Si exhibits many promising characteristics, such as the abundance of its constituent elements in the earth's crust and the non-toxicity of its processing by-products, resulting in freedom from concerns regarding prospective extended restrictions on hazardous substances. The efficiency of a thermoelectric device is characterized by the dimensionless figure of merit, ZT. It is well known that several kinds of dopants are effective in improving the thermoelectric performance of n-type Mg₂Si. With Bi-doped n-type Mg₂Si, we have achieved a maximum value of the dimensionless figure-of-merit ZT of ~1.0 at ~850 K. However, the correlation between the ZT values and the power generation characteristics, which is essential to understand in order to design a structure for a TE power generation module, has not been sufficiently investigated. In order to design a structure for a thermoelectric module using Mg₂Si, we examined the correlation between the ZT values and the power-output of a single element using Mg₂Si (ZT = 0.6) and Mg₂Si doped with donor impurities such as Al and/or Bi (ZT = 0.65~0.73). The measured single element was 2x2 mm² in section and 10 mm long. Additionally, we developed and evaluated a new architecture based on a 'unileg' structure Mg₂Si TE power generation module, which can improve the module lifetime and simplify its manufacture. As a starting material for the fabrication of the single element and the TE modules, pre-synthesized polycrystalline Mg₂Si, fabricated by UNION MATERIAL was used. The material was sintered using a plasma-activated sintering (PAS) technique, and, at the same time, Ni electrodes were formed on the Mg₂Si by employing of a monobloc PAS technique. The thermoelectric power-outputs were measured under a temperature difference, ΔT, ranging from 100-to-500 K by using UNION MATERIAL UMTE-1000M. The observed power-output for single element of Mg₂Si (ZT = 0.6), 2 at % Bi-doped Mg₂Si (ZT = 0.65) and 1at % Bi + 2at % Al-doped Mg₂Si (ZT = 0.73) were 5 mW, 1.7 mW and 2.0 mW respectively at ΔT = 500 K (between 873 K and 373 K). For the new architecture based on the unileg structure thermoelectric module, the observed value for power-output-per-unit-area was 1.0 mW/mm² at ΔT = 500 K (between 873 K and 373 K).

N3.18

Decoupling of Electric and Thermal Transport in Manganite Films by Polaron Ordering. Christian Jooss, Stefanie Wiedigen and Joerg Hoffmann; Institute of Materials physics, University of Goettingen, Goettingen, Germany.

Complex oxides like manganites represent a class of thermoelectric materials with high potential for application due to chemical and thermal stability at elevated temperatures. These materials have large Seebeck coefficients but unfortunately, relatively low ZT~0.02 because of their poor electric conductivities. Doping improves the conductivity but counteracts the Seebeck coefficient. Therefore, simple monolithic materials optimization is not promising and a route for enhancing ZT to values larger than 1 seems to be only possible in nanostructures and multilayer system. In this contribution we consider the impact of small polaron conduction on the thermoelectric properties in the strongly correlated manganite system Pr_{0.7}Ca_{0.3}MnO₃ with large electron-phonon coupling. We demonstrate that a polaron solid-liquid transition at hetero-interfaces of this manganite system can be induced by electric stimulation [1]. This allows for manipulation the ratio between electric and thermal conductivities in manganite-metal and manganite-oxide heterostructures and thus represents a new route for the design of thermoelectric devices by tuning in external fields. The experiments have been performed at various metal-PrCaMnO and oxide-PrCaMnO heterostructures (metal = Ag, Au, Pt, oxide = ITO, YBaCuO) which are prepared by ion beam sputtering. We discuss possible mechanisms for the decoupling of thermal and electric transport by polaron ordering and a related soft phonon mode. [1] Ch. Jooss, J. Hoffmann, J. Fladerer, M. Ehrhardt, T. Beetz, L. Wu, and Y. Zhu Phys. Rev. B 77 (2008) 132409

N3.19

Fabrication Process and Power Generation Characteristics of the Micro Thermoelectric Devices Composed of n-type Bi-Te and p-type Sb-Te Nanowires Min-Young Kim, Kyung-Won Park and Tae-Sung Oh; Materials Science and Engineering, Hongik University, Seoul, Korea, South.

Micro thermoelectric devices were processed by electroplating of the n-type Bi-Te nanowires and p-type Sb-Te nanowires into of an alumina template with 200 nm pores. The thickness and the area dimension of the alumina template where the Bi-Te or the Sb-Te nanowire device was formed were 50 μm and 5 mmX5mm, respectively. Power generation characteristics of the micro devices composed of the Bi-Te nanowires, the Sb-Te nanowires, and both the Bi-Te and the Sb-Te nanowires were characterized with applying a temperature difference of 40°C across the devices along the thickness direction. The n-type Bi-Te and the p-type Sb-Te nanowire devices exhibited thermoelectric power outputs of 3.8×10^{-10} W and 4.8×10^{-10} W, respectively. Such small output powers of the nanowire devices might be attributed to improper contact between the nanowire array and the upper electrode. The output power of the device composed of both the Bi-Te and the Sb-Te nanowires decreased to 1.4×10^{-10} W due to a large electrical resistance of the Cu electrode connecting the Bi-Te nanowire array with the Sb-Te nanowire array.

N3.20

Processing and Thermoelectric Characteristics of the Thermopile Sensors Composed of the Electrodeposited p-type Sb-Te and n-type Bi-Te Films Min-Young Kim, Jung-Yeol Choi and Tae-Sung Oh; Materials Science and Engineering, Hongik University, Seoul, Korea, South.

MEMS technologies have realized various sensors with high sensitivity, small size and new functions. One of such MEMS sensors is a thermal sensor which can detect environmentally harmful substances by converting a thermal energy generated by chemical reaction into electrical signal. Among various thermal sensors, thermopile sensors using Seebeck effect generate a voltage with a temperature difference and have several advantages such as high sensitivity and miniaturization. Recently, various works have been performed to utilize thermoelectric semiconductors with high Seebeck coefficients as thermopile films. Bi₂Te₃ and Sb₂Te₃ are narrow band-gap semiconductors with superior thermoelectric characteristics at room temperature and possess promising applications for thermopile sensors. In this study, thermoelectric properties of the electrodeposited p-type antimony-telluride (Sb-Te) and n-type bismuth-telluride (Bi-Te) films were evaluated with variations of the composition and the film thickness to optimize the Seebeck coefficient and the power factor of the films. A thermopile sensor was processed on a glass substrate with electrodeposition of the p-type Sb-Te and the n-type Bi-Te thin-films. A thermal sensor composed of 196 pairs of the Sb-Te and the Bi-Te thin-film legs exhibited a thermal sensing capability of 7.3 mV/K.

N3.21

Thermoelectric Properties of Sb-doped Sintered Mg₂Si Fabricated using Commercial Polycrystalline Sources. Naoki Fukushima¹, Tsutomu Iida¹, Masayasu Akasaka², Takashi Nemoto³, Ryo Kobayashi¹, Yoshifumi Takanashi¹ and Keishi Nishio¹; ¹Tokyo University of Science, Noda-shi, Japan; ²Dow Corning Toray Co.,Ltd., Ichihara, Japan; ³Nippon Thermostat Co.,Ltd., Kiyose-shi, Japan.

Magnesium silicide (Mg₂Si) has been identified as a high-performance thermoelectric material that covers the temperature range from 500 to 800 K, and one that fits well with the operating temperatures of automobile exhausts, incinerators and boilers. The important features of Mg₂Si include the fact that it has been identified as an environmentally-friendly material, that its constituent elements are abundant in the earth's crust, and that it is non-toxic. Although thermoelectric devices have obvious merits in terms of power generation, one of the reasons why thermoelectric devices are not more widely used at present is that the cost-per-watt of thermoelectric power generation has been too high to allow it to displace existing technologies. Mg₂Si has significant advantages for automobile applications in terms of both lower raw materials costs due to the abundance of its constituent elements, and its lighter weight compared with conventional thermoelectric materials such as Bi₂Te₃ and CoSb₃. It is necessary to dope the raw material in order to optimize the thermoelectric properties of Mg₂Si for practical applications, and typical device operating temperatures require high stability from any substitutional elements that are used as dopants. Aluminum (Al), Bismuth (Bi) and Antimony (Sb) are well known as n-type dopants for Mg₂Si. Antimony is considered to be a dopant that substitutes more stably into Si-sites in Mg₂Si compared with the other elements by a first principle calculation. The doping characteristics of Sb for as-grown Mg₂Si crystals or for Mg₂Si sintered directly from Mg and Si sources by solid-phase diffusion have been reported in an earlier study. We have now tried to sinter Mg₂Si from pre-synthesized sources in order to obtain a homogeneous composite that includes Sb. The pre-synthesized commercial poly-crystalline Mg₂Si sources were provided by UNION MATERIAL CO., LTD. and the doping ratios of Sb were varied between 0.5, 1.0, 2.0, and 3.0 at.%. The polycrystalline Mg₂Si sources were pulverized and then sintered using a Plasma Activated Sintering (PAS) technique. The sintered samples were characterized by XRD, and the results indicated that Mg₂Si was successfully formed. In order to evaluate the fundamental electrical properties of the material, Hall carrier concentration and Hall mobility were measured by the van der Pauw method. For the thermoelectric properties, the Seebeck coefficient and the electrical conductivity were evaluated using ULVAC-RIKO ZEM-2 equipment, while the thermal conductivity was evaluated by the laser flash method. In conjunction, we are also working on the formation of Ni electrodes on Mg₂Si by monobloc sintering in order to extract the generated output power. In this report, we will discuss the thermoelectric properties of these samples and will evaluate the output power of the samples fabricated with electrodes.

N3.22

Enhancement of Transverse Thermoelectric Power Factor in Bi/Cu Multilayer. Tsutomu Kanno, Satoshi Yotsuhashi, Akihiro Sakai, Kouhei Takahashi and Hideaki Adachi; Advanced Technology Research Laboratories, Panasonic Corporation, Kyoto,

Japan.

In anisotropic materials, transverse thermoelectric voltage is generated in the direction perpendicular to applied temperature gradient. We have investigated transverse thermoelectric effect in tilted Bi/Cu multilayer by calculation as well as experiment. Firstly, using tensorial representation along with an equivalent circuit model, we evaluated transverse thermoelectric power factor (PF) as a function of relative thickness of Cu and tilt angle between multilayer and element surface. We found that transverse PF exceeding $100 \mu\text{W}/\text{cm}\cdot\text{K}^2$ is possible by selecting appropriate device parameters (tilt angle of 30° and relative thickness of Cu more than 85 %), while conventional PF of constituent Bi is $33 \mu\text{W}/\text{cm}\cdot\text{K}^2$ at room temperature. Secondly, we developed a 2D finite element model using ANSYSTM software. It was clarified that transverse thermoelectric voltage is generated by inhomogeneous temperature distribution due to the difference in thermal conductivity of Bi and Cu. Finally, we fabricated tilted Bi/Cu multilayer by pressure-injection of molten Bi into a periodically slitted Cu block and subsequent cutting. The sample size, layer thickness and tilt angle were $26 \times 5 \times 10 \text{ mm}^3$, $0.24 \text{ mm} : 0.56 \text{ mm}$ (3:7) for Bi:Cu and 30° , respectively. Electrodes were prepared on $5 \times 10 \text{ mm}^2$ faces and temperature gradient was applied across $26 \times 10 \text{ mm}^2$ faces. Electrical resistivity was $15 \mu\Omega\cdot\text{cm}$ and transverse Seebeck coefficient was up to $27.4 \mu\text{V}/\text{K}$ after eliminating the contribution by electrodes. Consequently, transverse thermoelectric PF was evaluated to be $50.1 \mu\text{W}/\text{cm}\cdot\text{K}^2$, which is approximately 1.5 times greater than conventional PF of constituent Bi. Devices utilizing transverse thermoelectric effect have an advantage to promote heat flux because electrodes can be configured without parasitic thermal losses. Low device heat resistance concomitant with high material power factor using the present artificial multilayer can offer new possible application for waste heat recovery system, for example, embedded in existing heat exchangers in factories.

N3.23

Development of $\text{Al}_2\text{O}_3\text{-ZnO}/\text{Ca}_3\text{Co}_4\text{O}_9$ Module for Thermoelectric Power Generation. Paolo Mele, Kaname Matsumoto, Takeshi Azuma, Keita Kamezaki, Saburo Tanaka and Jun-ichiro Kurosaki; Materials Science and Engineering, Kyushu Institute of Technology, Kitakyushu, Japan.

Thermoelectric materials, that can convert waste heat into electrical energy, will play an important role in the current challenge to develop alternative energy technologies to reduce our dependence on fossil fuels and reduce greenhouse gas emissions. One of the most fascinating challenges of the material science is to develop high-performance and low-cost thermoelectric materials for practical applications. We present here the thermoelectric properties of $\text{Al}_2\text{O}_3\text{-ZnO}$ (n -type) and $\text{Ca}_3\text{Co}_4\text{O}_9$ (p -type) n -type and p -type materials and we will discuss the characteristics of modules prepared assembling these materials. Sintered pellets were prepared starting from the oxides. In the case of n -type, ZnO and Al_2O_3 nano-powders were weighted in proper stoichiometric amounts to obtain 0 mol%, 2 mol%, 5 mol% and 8 mol% Al_2O_3 doped ZnO. The reagents were mixed by means of ZrO_2 balls with EtOH for 6h, then dried at 80°C for 24h. The dried mixtures were subjected to a preliminary sintering treatment at $T' = 1000^\circ\text{C}$ for 8h, then remixed again in the same conditions used at the beginning. Finally, 25 mm Φ pellets were isostatically pressed and sintered at $T'' = 1400^\circ\text{C}$ for 8h. In the case of p -type, CaO and Co_3O_4 were weighted in stoichiometric amounts to obtain $\text{Ca}_3\text{Co}_4\text{O}_9$. The synthesis procedure was the same used for $\text{ZnO}+\text{Al}_2\text{O}_3$ pellets, however $T' = 600^\circ\text{C}$ and $T'' = 960^\circ\text{C}$. The sintered pellets were cut by a diamond saw in a pillar shape ($20 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$) for following experimental checks. Crystal phase was determined by XRD. Seebeck coefficient (S) and electrical conductivity (σ) were measured in the range $100^\circ\text{C} - 800^\circ\text{C}$ by means of ZEM-1 while thermal conductivity (κ) was checked by Ω -3. The best doped sample was 5 mol% Al_2O_3 ZnO showing $S = -160 \mu\text{V}/\text{K}$ and $\sigma = 38 \text{ S}/\text{cm}$ at 800°C , while $\kappa = 4.78 \text{ W}/\text{m}\cdot\text{K}$ at 600°C . Typical values for $\text{Ca}_3\text{Co}_4\text{O}_9$ were $S = 82.5 \mu\text{V}/\text{K}$ and $\sigma = 98 \text{ S}/\text{cm}$ at 800°C , while $\kappa = 1.01 \text{ W}/\text{m}\cdot\text{K}$ at 600°C . n -type and p -type pellets were cut in small pieces ($10 \text{ mm} \times 1 \text{ mm} \times 1 \text{ mm}$) that were electrically connected in series to the generation of thermoelectric voltage. Couples of n -type and p -type elements were stuck on Ag electrodes ($10 \text{ mm} \times 10 \text{ mm}$) by silver paint. The n - p couples were then connected by Ni wires and heated from the bottom on a hot plate (T_{MAX} up to 300°C). The voltage and temperature were monitored by a PC equipped by Labview software. Several modules were fabricated increasing the number of connected couples up to 5. A fin was placed on the top of the elements to keep a ΔT between the elements' ends. The best performance was obtained in the module formed by 5 mol% $\text{Al}_2\text{O}_3/\text{Ca}_3\text{Co}_4\text{O}_9$ couples, that generated a voltage $V = 19 \text{ mV}$ at 200°C (when $\Delta T = 100^\circ\text{C}$). We are looking forward to enhance the performance of modules achieving a figure of merit $\sigma^2 S = ZT = 1$, or higher, especially by increasing the electrical conductivities of ZnO and $\text{Ca}_3\text{Co}_4\text{O}_9$. Acknowledgement Members of Thermal Device Laboratory in KIT are gratefully acknowledged for their support in module's making.

N3.24

Abstract Withdrawn

N3.25

Evaluation of Measurement Thickness In Distribution Evaluation Instrument using Thermal Probe. Satoaki Ikeuchi¹, Maho Yoshiizumi¹, Kenji Shimada¹, Youichi Takasaki¹, Yoshikazu Ishii¹ and Atsushi Yamamoto²; ¹ULVAC-RIKO, Inc., Yokohama, Japan; ²Energy Technology Research Institute, National Institute of Advanced, Tsukuba, Japan.

To develop thermoelectric materials with the high performance, thermoelectric materials consisting of multi elements have been synthesized. Thermoelectric material with complicated composition will be composition and carrier distributions. Their performance of those materials, which depends on Seebeck coefficient, thermal conductivity and electric resistivity, have the

distributions. We have been developing Scanning Thermal Probe Micro-image (STPM) which can measure the distribution in local area by using the thermal probe. Seebeck coefficient and thermal conductivity distributions are evaluated at the same time. We assume that some heat obtained from the heated thermal probe does not reach to the rear surface in the sample. In such a thin sample, the heat reaches to the rear surface so that the temperature for the rear surface rises. In this condition, the result involves the contribution of besides thin sample. In this work, to clear the limit of the thickness in the sample, we measured by using STPM in $(\text{Bi}_2\text{Te}_3)_{0.15}(\text{Sb}_2\text{Te}_3)_{0.85}$ at 0.2 mm, 0.4 mm, 0.8 mm, 1.0 mm, 1.5 mm and 2.0 mm. Both values of the Seebeck coefficient and thermal conductivity were evaluated as the average of results in 400 points. These values were not affected by the temperature rise for the rear surface. This shows that, when thermal conductivity in the sample is below $2 \text{ W m}^{-1} \text{ K}^{-1}$, Seebeck coefficient and thermal conductivity can be evaluated above 0.2 mm in thickness.

N3.26

Abstract Withdrawn

N3.27

Synthesis and Characterization of Doped and Undoped PbTe Nanocomposites. Hillary Kirby¹, J. Martin^{1,3}, L. Chen² and George S. Nolas¹; ¹Physics, University of South Florida, Tampa, Florida; ²Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China; ³Ceramics Division, NIST, Gaithersburg, Maryland.

Lead telluride (PbTe) nanocomposites with varying carrier concentrations were prepared from Na and Ag doped and undoped PbTe nanocrystals synthesized utilizing an alkaline aqueous solution-phase reaction. This procedure reproducibly synthesizes 100-150 nm crystals with a high yield of over 2 g per batch. The nanocrystals were then subject to Spark Plasma Sintering (SPS) for densification. Transport properties were evaluated through temperature dependent resistivity, Hall, Seebeck coefficient, and thermal conductivity measurements. These measurements were compared to bulk polycrystalline lead tellurides with similar carrier concentrations. The potential for thermoelectric applications is also investigated.

N3.28

Fabrication and Characterization of Bi₂Te₃ Nanoparticle-Polythiophene Nanocomposite for Thermoelectric Materials. Chang-Chung Yang¹, I-Hsiang Lo² and Chao-Chin Chang²; ¹Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan; ²Department of Chemical and Materials Engineering, Tamkang University, Taipei, Taiwan.

The thermoelectric performance of a material could be evaluated by its figure of merit ZT which is consisted of Seebeck coefficient, electric conductivity, thermal conductivity and applied temperature. The ZT of the thermoelectric materials has approached the value of 1 in the 1960s, but does not have the significant breakthrough until the recent decade. In 1993, Mildred S. Dresselhaus proposed a new concept that the low-dimensional materials could have improved ZT and brought a hope to thermoelectric materials. In this study, we used this concept to prepare nanocomposites for thermoelectric materials. Here we proposed a new thermoelectric material by composite engineering, which was composed of conducting polymers and the conventional thermoelectric materials. Since the conventional thermoelectric materials have good electric conductivity and Seebeck coefficient, the conducting polymers with low thermal conductivity could increase the phonon scattering to ruin the thermal transportation in the prepared composites and maintain their electric properties. The thermoelectric performance could be adjusted by composite engineering. We chose the conducting polythiophene P3HT and the thermoelectric material Bi₂Te₃ which owned the best ZT at room temperature. In order to improve the miscibility between P3HT and Bi₂Te₃, firstly, we synthesized the protection agent 3-MHT with similar structure of P3HT to prepare Bi₂Te₃ nanorods. The protection agent 3-MHT identified by ¹H-NMR and FTIR could fabricate Bi₂Te₃ nanorods with 350~1500 nm in length and 25~150nm in diameter dependent on their experimental parameters. TEM, XRD and EDS results identified and characterized Bi₂Te₃ nanorods correctly. The Bi₂Te₃ nanorods capped with 3-MHT guaranteed their miscibility with P3HT polymers. Secondly the designed nanocomposites were manufactured by a simple mixing of Bi₂Te₃ nanorods and P3HT polymer in solution. TEM image demonstrated a well-dispersed morphology of the Bi₂Te₃ nanorods in P3HT polymer matrix. We measured the band-gap, electric conductivity and Seebeck coefficient of the prepared nanocomposites but the electric properties were not good as expectancy due to the electric-insulating protection agent 3-MHT. The addition of Bi₂Te₃ nanorods led to worse electric conductivity from 218 S/m, the value of pristine P3HT polymers, to 76~113 S/m and the Seebeck coefficient slightly increased from 32 $\mu\text{V/K}$ to 37~39 $\mu\text{V/K}$. The best ZT was estimated to be the value of 0.045 for the prepared P3HT-Bi₂Te₃ nanocomposites.

N3.29

The Preparation of Donor-Acceptor Type Narrow Band Gap Poly(thieno[3,4-b]pyrazine) Derivatives and their Applications on Thermoelectrics. Chang-Chung Yang¹, Po-Ju Huang², Hong-Cheu Lin², Ming-Shan Jeng¹ and Ya-Wen Chou¹; ¹Energy and Environment Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan; ²Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

Organic thermoelectric materials are still new materials in the field of thermoelectrics and have the potential to find smart application on soft electronic cooling or small scale power generation using low-temperature waste heat. In this research, the novel conjugated poly(thieno[3,4-b]pyrazine) derivatives with narrow band gap (Eg) have been prepared to investigate the application on thermoelectrics. The useful thermoelectric polymers have some criteria to obey. One of these criteria, the low band gap polymers that have intrinsic electric conductivity can use different oxidizing dopant to increase the hole concentration and the

hole mobility. In our synthetic strategy, we used the donor(D)-acceptor(A) system and fusing ring system of precursors to synthesize the low band gap polymers. When the donor and acceptor moieties were introduced on the main chain of polymers, the highest occupied molecular orbital (HOMO) levels of donors and the lowest unoccupied molecular orbital (LUMO) levels of acceptors would further hybridize to reduce the band gap. Therefore, in order to lower the band gap efficiently, the stronger electron-accepting and the stronger electron-donating moieties were necessary. The stronger D-A interaction between consecutive repeating units in the conjugated polymers could make the main chain coplanar to increase the delocalizing capability of π -electron and the possibility of electron-hopping between the main chains of polymers due to their good packing. In this research, the donor is 4,4-dialkylcyclopentadithiophene and the acceptor is thieno[3,4-b]pyrazine. The different doping conditions were optimized the power factor and investigated the thermoelectric behavior of the polymers. In order to increase the conductivity, different dopant, like I₂ and FeCl₃, and doping condition were used. The maximum conductivity of copolymer measured by home-made instrument is 1.5 S/cm due to its low band gap and non-substitution on the thieno[3,4-b]pyrazine. The effective conjugation length of copolymers with longer substitutes on the thieno[3,4-b]pyrazine were reduced to lower the conductivity. When the conductivity of material increases, their Seebeck coefficient decreases generally. The Seebeck coefficient is in the range of +17.3 to +238.8 μ V/K. The positive coefficient demonstrated the p-type carrier behavior. The power factor ($S^2\sigma$) is major contribution to the figure of merit of thermoelectric property ($ZT = S^2\sigma T/\kappa$). The value of power factor is between 2.5×10^{-9} and 6.7×10^{-8} W/m-K². These values are still too poor to have any reasonable application. The following research would focus on theoretical simulation on the potential Seebeck coefficient of conjugated polymer with high electric conductivity.

SESSION N4: Nanocomposites and Nanostructured Materials II

Chairs: Harald Bottner and Ryoji Funahashi

Wednesday Morning, April 15, 2009

Room 2010 (Moscone West)

8:30 AM N4.1

Understanding Electrical Transport and the Large Power Factor Enhancements In Co-Nanostructured PbTe. Joseph Sootsman¹, Vladimir Jovicic², Christopher M Jaworski², Joseph P Heremans², Jiaqing He³, Vinayak P Dravid³ and Mercouri G Kanatzidis¹; ¹Department of Chemistry, Northwestern University, Evanston, Illinois; ²Department of Mechanical Engineering, Ohio State University, Columbus, Ohio; ³Department of Materials Science, Northwestern University, Evanston, Illinois.

Thermoelectric materials hold promise in waste heat to electrical power generation and could play a role in future energy management if their efficiency can be improved. Primarily, recent enhancements in thermoelectric figure of merit have come from reduction in the thermal conductivity in nanostructured materials. However, we recently reported the synthesis and characterization of PbTe nanostructured with both Pb and Sb precipitates which has an increased figure of merit. The combination of these precipitates caused unexpected changes in the electron mobility resulting in higher than expected power factors at high temperature. These enhanced power factors coupled with a reduced thermal conductivity resulted in ZT values approaching 1.4 at 675K. Additional transport measurements to determine the scattering parameter, high temperature transmission electron microscopy, and three-dimensional atom probe tomography results will be reported with the hope of elucidating the mechanism of this novel transport behavior.

8:45 AM N4.2

Tailoring Thermoelectric Properties of Segregated-network Polymer Nanocomposites for Thermoelectric Energy Conversion. Dasaroyong Kim, Yeonseok Kim, Jaime C Grunlan and Choongho Yu; Mechanical Engineering, Texas A&M University, College Station, Texas.

Polymers are intrinsically poor thermal conductors, which are ideal for thermoelectrics, but low electrical conductivity and thermopower have excluded them as feasible candidates as thermoelectric materials in the past. However, recent progresses in polymer technology, particularly nanomaterial-polymer composites can bring them into degenerate semiconductor or metallic regimes by incorporating a small amount of conductive fillers. Here, we demonstrate that such polymer nanocomposites can be viable for light-weight and economical thermoelectrics by using a segregated network approach for the nanocomposite synthesis. In the case of 20 wt% CNT polymer composite films made of PVAc matrix, a thermoelectric figure of merit was measured to be 0.006 at room temperature. The thermoelectric properties were further improved by replacing PVAc with electrically conductive polymers including Poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) doped with dimethyl sulfoxide (DMSO). The influence on thermoelectric properties from filler concentration, matrix materials, and stabilizer materials are also discussed.

9:00 AM N4.3

Enhancement of Thermoelectric Figure-of-Merit by a Nanostructure Approach. Zhifeng Ren¹, Bed Poudel^{2,1}, Yi Ma^{1,2}, Yucheng Lan¹, Xiaowei Wang¹, Giri Joshi¹, Gaohua Zhu¹, Jian Yang¹, Bo Yu¹, Xiao Yan¹, Dezhi Wang¹, Qing Hao³, Hohyun Lee³, Austin Minnich³, Andrew Muto³, Daryoosh Vashaee³, Xiaoyuan Chen³, Gang Chen³, Junming Liu⁴ and Mildred S Dresselhaus⁵; ¹Physics, Boston College, Chestnut Hill, Massachusetts; ²GMZ Energy Inc., Newton, Massachusetts; ³Department of Mechanical Engineering, MIT, Cambridge, Massachusetts; ⁴Department of Physics, Nanjing University, Nanjing, China; ⁵Department of Physics, MIT, Cambridge, Massachusetts.

The dimensionless thermoelectric figure-of-merit (ZT) in bulk materials has remained about 1 for many years. Here we show that a significant ZT improvement can be achieved in nanocrystalline bulk materials. These nanocrystalline bulk materials were made by hot-pressing nanopowders that are ball-milled from either crystalline ingots or elements. Electrical transport measurements,

coupled with microstructure studies and modeling, show that the ZT improvement is the result of low thermal conductivity caused by the increased phonon scattering by grain boundaries and defects. More importantly, the nanostructure approach has been demonstrated in a few thermoelectric material systems, proving its generality. The approach can be easily scaled up to multiple tons. Thermal stability studies have shown that the nanostructures are stable at the application temperature for an extended period of time. It is expected that such enhanced materials will make the existing cooling and power generation systems more efficient.

9:30 AM *N4.4

Nanosized Granular Boundaries in Polycrystalline Pb_{0.75}Sn_{0.25}Te: An Innovative Approach to Enhancing the Thermoelectric Figure of Merit. Jian He, Xiaohua Ji, Bo Zhang, Zhe Su, Tim Holgate and Terry M Tritt, Physics and Astronomy, Clemson University, Clemson, South Carolina.

Most of the recent advances in enhancing the dimensionless thermoelectric figure of merit ZT are linked to the thermal conductivity reduction. As the heat-carrying phonons are widely dissipated in the energy and momentum space, the structural complexity on the multiple length scales, especially at those comparable to the phonon wavelength, is necessary for the thermal conductivity reduction desired. In this work we utilized an Alkali metal (Na, K) hydrothermal treatment followed by hotpressing procedure to facilitate the formation of a nanosized granular grain boundary in the polycrystalline Pb_{0.75}Sn_{0.25}Te system. The presence of this rough grain boundary, whose mean roughness height and roughness period are on the order of several nanometers, results in a significant lattice thermal conductivity reduction without appreciably affecting the thermopower or the electrical resistivity. As a result, a ZT ~ 0.50 (0.38) has been attained in the Na (K)-processed sample at ~ 425 K (475 K), as compared to the ZT ~ 0.34 at ~ 490 K in the bulk reference sample. The present work provides a novel avenue by which the lattice thermal conductivity of a polycrystalline system can be decoupled from the electronic properties via controlling the micro-morphology of the grain boundary.

10:30 AM *N4.5

Metal-semiconductor Nanocomposites for Thermoelectric Energy Conversion. Ali Shakouri, Univ. of California Santa Cruz, Santa Cruz, California.

We will review the potential of metal-semiconductor multilayers and embedded nanoparticles for thermoelectric energy conversion. Theoretical calculations of the electrical conductivity, Seebeck coefficient and the electronic contribution to thermal conductivity using Boltzmann equation is presented. Corrections due to superlattice minibands and nanoparticle scattering show the role of hot electron energy filtering. Finite particle sizes in couple of nanometer range require the use of partial wave technique in estimating the scattering cross sections. In addition, coherent potential approximation is used to include multiple scatterings at high concentrations of nanoparticles. Theory and experiment are compared in the case of rare-earth ErAs nanoparticles in InGaAlAs semiconductor matrix. Experimental in-plane electrical conductivity and Seebeck coefficient are obtained in 300-800K range. The cross-plane electrical conductivity, Seebeck coefficient and thermal conductivity of 20 microns thick films are extracted using transient Harman technique and thermal imaging of single leg micro refrigerators. Preliminary theoretical calculation and experimental characterization of ZrN/ScN multilayer films are also presented. Potential to reach ZT values exceeding 2-3 are discussed.

11:00 AM *N4.6

Skutterudite-based Thermoelectrics: Nano-composites and Device Development. Lidong Chen, Wenqing Zhang, Xiaoya Li and Xiangyang Huang; Institute of Shanghai Ceramics, CAS, Shanghai, China.

Thermoelectric (TE) conversion receives great attention as a prospective energy conversion technique such as in the harvest of solar energy and recovery of industrial exhausted heat. Recently, significant progress in both material research and device development has been achieved world-wide. This review will provide a summary of some effective techniques for improving TE performance through multi-level microstructure control with focusing on the skutterudite-based materials. A proven approach to elevate figure of merit (ZT) is via formation of nano-composites, in which extrinsic nano-phases are dispersed at grain boundaries and/or within grain. Acting as energy filter and phonon scattering center, nano-phases contribute to both the increase of thermopower and the reduction of thermal conductivity without much degradation of electrical conductivity. The distribution state of the extrinsic phase, including the content, homogeneity and structures, are the key factors for the enhancement of ZT value of the composites. Several novel approaches including in-situ reaction, vapor-transportation and sol-gel process to prepare TE composites with dispersion of extrinsic nano-particles have been developed. The thermal stability of the nano-structure was studied. The design and fabrication of TE device using high performance skutterudite materials have also been carried out using Mo-based alloys as electrode. The interfacial microstructure of the skutterudite/electrode joints were found to give very critical influences on the interfacial electrical resistivity and thermal resistivity and bonding strength, and therefore to give great influence on thermoelectric performance. Some novel processes for fabricating skutterudite/electrode joints have been developed. The reliability and life duration behavior of the TE device have also been studied with focusing on the microstructure evolution during the accelerated test. Some criteria on the development of high performance TE device using skutterudite materials will be also discussed in this report.

11:30 AM N4.7

Thermal Transport in Rough Silicon Nanowires for Thermoelectric Applications Sanjiv Sinha¹, Bair Budaev² and Arun Majumdar^{2,3,4}; ¹Mechanical Science & Engineering, University of Illinois, Urbana, Illinois; ²Mechanical Engineering, University of California, Berkeley, California; ³Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California;

⁴Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, California.

Recently reported data on electrolessly etched rough silicon nanowires [1] suggest a hundredfold increase in ZT due to reduction in thermal conductivity of the same order. However, no known theoretical model for thermal conductivity of crystalline dielectrics predicts such reduction. Further, the observed linear increase in thermal conductivity with temperature in nanowires with diameters approaching 50 nm defies the widely-accepted Klemens-Callaway [2] model of thermal conductivity for silicon. Here we discuss a new model that considers the wave-like transmission of acoustic phonons through the wire. We show that such a nanowire behaves in essence, like a waveguide with the resulting wave dispersion becoming size and roughness dependent. Considering a two-dimensional analogue of the wire problem, we solve the Helmholtz wave equation for acoustic waves in a rough film [3]. We show that roughness leads to a coupling of different modes and also the conversion of propagating modes to evanescent modes. This conversion to evanescent localizes phonons in wires with localization lengths approximately greater than a micrometer. We compute the resulting thermal conductivity of rough Si nanowires and show good comparison with experimental data. 1. A.I. Hochbaum et al., Nature 451, 163-167 (January 2008). 2. G. A. Slack, Solid State Physics, 34, 1, Academic Press, New York (1969). 3. V.D. Freilikher et al., Radiofizika, 13, 73, 1972.

11:45 AM **N4.8**

Vacuum Thermionic Energy Conversion Based on Nanostructured Doped Diamond Thin Films. Franz A Koeck¹, Robert J Nemanich¹ and Ken Haenen²; ¹Department of Physics, Arizona State University, Tempe, Arizona; ²Institute for Materials Research, Hasselt University, Diepenbeek, Belgium.

Vacuum thermionic energy conversion is a process where thermally activated electrons from an emitter traverse a vacuum gap and are collected by a counter - electrode. Closing the circuit to the emitter establishes an electrical current where electrons can do work in external devices. Key component of a vacuum energy converter is an efficient electron source which can sustain an electron current at low to moderate temperatures. The electron emission current described by the law of Richardson - Dushman relates emission barrier or work function and emission constant to materials properties. Diamond based emitter configurations can exploit material aspects by means of controlling dopants as well as structural characteristics. By identifying suitable donors a low effective work function material can be synthesized. For nitrogen and phosphorus doped films we have measured work functions of 1.3 eV and < 1 eV, respectively. Here, the effective work function is dependent on surface termination, i.e. negative electron affinity which also alleviates system detrimental space charge effects. In order to obtain significant emission current densities a nitrogen - incorporated ultra - nanocrystalline diamond film (UNCD) was utilized as an interstitial layer between substrate and doped diamond film. This resulted in electron emission commencing at temperatures < 250 °C with a significant value for the Richardson's constant. High temperature operation in excess of 700 °C was indicative of stable film and surface properties for phosphorus - doped diamond films. In a vacuum thermionic converter configuration nitrogen - incorporated UNCD based emitter and collector structures provided a significant open source voltage of ~ 0.4 V at a moderate temperature of 500 °C. This research is supported by the TEC-MURI project.

SESSION N5: Theory
Chairs: Jian He and Ali Shakouri
Wednesday Afternoon, April 15, 2009
Room 2010 (Moscone West)

1:30 PM **N5.1**

First Principles Study of Metal/Bi₂Te₃ Interfaces: Implications to Improve Contact Resistance. Ka Xiong¹, Weichao Wang¹, Husam N Alshareef¹, Rahul P Gupta¹, Bruce E Gnade¹ and Kyeongjae Cho^{1,2}; ¹Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas; ²Physics, University of Texas at Dallas, Richardson, Texas.

To allow the thermoelectric coolers to reach the next level of performance in terms of efficiency and power density, a low contact resistance value is needed [1]. For current thermoelectric devices, electroless Ni has been used as the contact metal with a contact resistance of ~ 5x10⁻⁶ Ωcm². The contact resistance needs to be at least 10-100 times lower in order to maintain the device scaling [2]. The contact resistance arises from the formation of the Schottky barrier between the metal and the semiconductor, and the interface band alignment has not been systematically optimized yet. Therefore, it is necessary to understand the factors that control the Schottky barrier height between metal and thermoelectric material. Furthermore, our recent experimental data showed that for Ni contacts on Bi₂Te₃ a NiTe interfacial region is formed, while for Co contacts on Bi₂Te₃ the CoTe interfacial layer has not been observed. This observation indicates the importance of the chemical stability of the interface and interfacial layer formation. For the purpose of understanding detailed interface electronic structures, we use first principles calculations to investigate the interface chemistry of Ni/Bi₂Te₃ and Co/Bi₂Te₃ interfaces. We propose several methods to reduce the Schottky barrier height by forming controlled interfacial dipole layers, which can be achieved by introducing impurities into the interface [3] or inserting the interfacial layer between the metal and Bi₂Te₃ [4]. These methods have been previously applied on metal/oxide interfaces to control the band offsets. This study will help us to gain fundamental understanding on the contact resistance, and possible mechanisms to reduce it. This work is supported by the II-VI Incorporated Foundation. References [1] J. -P. Fleurial, Proc 18th Intl. Conf. on Thermoelectrics, pp294, Baltimore, USA (1999). [2] V. Semenyuk, Proc 20th Intl. Conf. on Thermoelectrics, pp391, Beijing, CHINA (2001). [3] K. Xiong et al. Appl. Phys. Letts. 92, 113504 (2008). [4] K. Xiong et al, J. Appl. Phys. 104, 074501 (2008).

1:45 PM **N5.2**

Studying the Power Factor of a Matrix with High Concentration of Embedded Nanoparticles. Mona Zebarjadi, Keivan

Esfarjani and Ali Shakouri; UC Santa Cruz, Santa Cruz, California.

In this presentation we investigate nanoparticle scattering effect on the thermoelectric transport properties using the average T-matrix approach and the coherent potential approximation (CPA). The two methods can have different predictions in the high concentration limit where multiple scattering is important. To include randomness in the nanoparticles sizes, we consider an effective medium for the electron scattering off of nanoparticles of different sizes using the CPA. Enhancement of the thermopower is investigated by looking at the slope of scattering cross section versus energy at the Fermi level. Effect of parameters such as nanoparticle size, height, concentration and the randomness of their distribution will be examined. The study will allow us to engineer nanoparticles with enhanced power factor.

2:00 PM **N5.3**

Enhanced Thermo-electric Transport of Strongly Correlated Electrons. Veljko Zlatić, Institute of Physics, Zagreb, Croatia.

We discuss the charge and heat transport of intermetallic compounds with Ce, Eu, and Yb ions using the periodic Anderson model in the limit of infinite correlation between the f electrons. We show that the normal state properties of the model are governed at low-temperatures by the Fermi liquid (FL) laws, with the characteristic energy scale T_0 . At high-temperatures, the model exhibits typical Kondo-like features that can be understood in terms of single impurity Anderson or Kondo models with Kondo scale T_K . Using the slave boson approach, we show that the values of T_0 and T_K depend on the shape of the conduction electrons density of states (c DOS) in the vicinity of the chemical potential, the degeneracy and the crystal field (CF) splitting of the f states, the number of c and f electrons, and their coupling. The crossover between the high-temperature incoherent regime and the low-temperature coherent one depends on the ratio T_0/T_K . Unlike in dilute alloys, this ratio is strongly system-dependent, which gives rise to different types of the crossover. We show that the low-temperature response is enhanced (or reduced) with respect to the predictions based on the single-impurity models that would lead to the same high-temperature behavior as the periodic Anderson model. We also show that the renormalization of transport coefficients in the coherent regime can invalidate the Wiedemann-Franz law and lead to an enhancement of the thermoelectric figure-of-merit. The FL laws explain the correlation between the specific heat coefficient $\gamma = C_V/T$ and the thermopower $\alpha(T)$, or γ and the T^2 coefficient of the electrical resistance $A = \rho(T)/T^2$. The FL laws of a N -fold degenerate model explain the deviations of the Kadowaki-Woods ratio $R_{KW} = A/\gamma^2$ and the q ratio, $q = |\lim_{T \rightarrow 0} \alpha/\gamma T|$, from the universal values. At high temperature, where $\alpha(T)$ and $\rho(T)$ exhibit large maxima, the perturbation theory shows that the overall temperature dependence of transport coefficients depends on the relative magnitude of T_K and the CF splitting Δ . To account for the effects of pressure or doping, we assume that they change the c - f coupling and T_K but not Δ . Using these results, we discuss the thermoelectric response of some typical heavy fermions and valence fluctuators. A sharp peak in the α at T_K , which explains the 'slow crossover' observed in YbAl_3 . The minimum in the ρ at T_K , which explains the abrupt transition between the high- and low-temperature regimes in YbInCu_4 . In the case of CeCu_2Ge_2 and CeCu_2Si_2 , where $T_0 = T_K$, we show that the pressure-dependence of the $A(P)$ coefficient and of the residual resistance is driven by the change in the degeneracy of the f states.

2:30 PM **N5.4**

Electronic and Vibrational Properties of Filled and Unfilled Ternary Skutterudites. Dmitri Volja², Fornari Marco¹, Boris Kozinsky³ and Nicola Marzari²; ¹Physics, Central Michigan University, Mt. Pleasant, Michigan; ²DMSE, Massachusetts Institute of Technology, Cambridge, Massachusetts; ³Research and Technology Center, Robert Bosch LLC, Cambridge, Massachusetts.

The renewed interest in unfilled and filled ordered ternary skutterudites, $\text{XCoAs}_{3/2}\text{B}_{3/2}$ (with A and B group IVB and VIB respectively, X a filler), spawns from the possibility to control details of the electronic and vibrational properties of such compounds. Recent experimental work pointed to significant changes in the transport properties with respect CoSb_3 : unfilled ternary tends to exhibit lower thermal conductivity but larger electrical resistivity [P. Vaqueiro and G. G. Sobany, Mater. Res. Symp. Proc. vol 1044 (2008)]. In order to explore optimization strategies for the electronic properties, we performed first principles band structure calculations for $\text{CoGe}_{3/2}\text{S}_{3/2}$, $\text{CoGe}_{3/2}\text{Te}_{3/2}$, and $\text{CoSn}_{3/2}\text{Te}_{3/2}$. In particular we have analyzed the details of the bonding using Wannier function approach as well as studied the electronic transport by a powerful band structure interpolation scheme. Within ab initio density functional perturbation theory we have computed the full phonon dispersions and analyzed the effect of filling with Ba. Our calculations point to a flattening of the bands around the Fermi level that results in larger energy gaps and effective masses especially for the valence band.

2:45 PM **N5.5**

The optimized Seebeck coefficient as a determinant of the maximum power factor in Silicon based bulk and nanostructured thermoelectrics Paothep Pichanusakorn and Prabhakar Bandaru; Materials Science program, Mechanical Engineering department, UC, San Diego, La Jolla, California.

The efficiency of thermoelectric devices is measured through the Figure of merit, $Z = (S^2\sigma)/(k_e + k_L)$, and is constituted from both electronic (the Seebeck coefficient: S , the electrical conductivity: σ , and the electronic part of the thermal conductivity: k_e) and lattice properties (lattice thermal conductivity: k_L). However, the electrical properties can vary by orders of magnitude and depend mainly on the carrier concentration. We show, through extensive analytical work and numerical simulations that there exists an

optimum reduced Fermi level (η_{opt}), where the power factor, $S^2\sigma$, is maximized, and which is largely independent of material, device geometry, and temperature. Consequently, given the relationship between S and η , we will show that there exists an optimal Seebeck coefficient, S_{opt} , which can now be set as a practical and direct measure for finding the optimal carrier concentration in any material at any temperature. We also consider the influence of the characteristic scattering exponent (r) in the range of -0.5 to $+1.5$. For example, given a constant relaxation time ($\tau=0$), S_{opt} in bulk material, quantum well, and quantum wire were calculated to be approximately 130, 167 and 186 $\mu\text{V/K}$, respectively. However, if acoustic phonon scattering is dominant, then S_{opt} is always equal to 167 $\mu\text{V/K}$. Given the optimum Fermi level and Seebeck coefficient, we then determine the minimum quantum well/wire thickness required to achieve an enhancement in $S^2\sigma$ over bulk values. We calculate that the minimum required quantum well and wire thickness for n-Si are both approximately 6.5 nm. We will also discuss the issue of breaking of valley degeneracy in nanostructures, which can reduce the power factor and cause major deviation from the ideal value.

3:30 PM N5.6

Experimental and Theoretical Studies of the Structure and Properties of Bulk Thermoelectric Bi-Te Compounds Alfredo Martin Morales¹, Monica Barney¹, Douglas L Medlin², Peter A Sharma², Catalin D Spataru², Ana L Lima Sharma³, Jian He⁴, Fivos Drymiotis⁴, Terry Tritt⁴ and James Turner⁴; ¹Materials Chemistry, Sandia National Laboratories, Livermore, California; ²Materials Physics, Sandia National Laboratories, Livermore, California; ³Department of Physics, Tuskegee University, Tuskegee, Alabama; ⁴Department of Physics and Astronomy, Clemson University, Clemson, South Carolina.

Bi_2 planes can be inserted into the parent Bi_2Te_3 structure—the most important commercial thermoelectric material—in order to form superlattice structures in a bulk material with the potential to increase thermoelectric efficiency. We have reported the synthesis, property measurements, and theoretical studies of Bi_2Te_3 , Bi_6Te_7 , BiTe , and Bi_2Te , and evaluated their potential for thermoelectric applications. Spark plasma sintering was found to be an effective way of eliminating porosity, which negatively affects the interpretation of the intrinsic properties. Superlattice formation has been confirmed using powder x-ray diffraction and TEM studies. Property measurements are consistent with the semimetallic nature of compounds with additional Bi_2 planes. A plausible explanation for the observed difference in thermal conductivity between Bi_2Te_3 and the other compounds could be that interface scattering becomes predominant when the phonon mean free path becomes comparable to the characteristic superlattice spacings. Electronic structure calculations have correctly obtained the structures and electronic nature (semimetallic versus semiconducting) of each compound. Bi_2Te_3 remains the best thermoelectric material in this series; however, Bi_2Te may warrant further investigation for refrigeration near 200 K. This work provides a firm foundation for understanding the role of superlattice formation and its effect on transport properties in a model bulk material that is amenable to a variety of microstructural, transport, and electronic structure studies.

3:45 PM N5.7

Direct and Indirect Effects of Filling on Band Structure and Phonon Dispersion of Skutterudites. Daehyun Wee¹, Boris Kozinsky², Marco Fornari³ and Nicola Marzari⁴; ¹Research and Technology Center, Robert Bosch LLC, Palo Alto, California; ²Research and Technology Center, Robert Bosch LLC, Cambridge, Massachusetts; ³Department of Physics, Central Michigan University, Mt. Pleasant, Michigan; ⁴Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Filled skutterudites are a promising class of medium to high-temperature thermoelectric materials. They exhibit low thermal conductivity, which is typically attributed to the phonon scattering process introduced by the filler. In recent years, however, the exact nature of the physical process involved in the reduction of the thermal conductivity and the associated rattling motion of the filler atom have been the subject of intense investigations and controversy. To provide better insights on the issue, we analyze the effect of filling $(\text{Co,Fe})\text{Sb}_3$ with various elements including alkaline earth metals on the band structure and on the full phonon dispersions, using state-of-the-art first principles calculations. In particular, we separate the effects of filler's mass, size, and electronic features on the vibrational spectrum. The effect that pressure has on the vibrational and electronic structure of skutterudite crystals is investigated, and anharmonic vibrational effects are explored by studying thermal expansion as a function of composition in the $\text{X}(\text{Co,Fe})\text{Sb}_3$ chemical space. We also present electronic transport coefficients estimated within the constant-relaxation-time approximation.

4:00 PM N5.8

Transport Properties of Thermoelectric Nanocomposites. Lilia M Woods, Adrian Popescu, Joshua Martin and George Nolas; Physics, University of South Florida, Tampa, Florida.

Transport properties of thermoelectric nanocomposite materials containing granular regions are considered. We present a model describing the carrier conductivity and Seebeck coefficient by taking into account the grain potential boundary scattering mechanism. Other mechanisms, such as carrier-acoustic phonon, carrier-non polar optical phonon, and carrier-impurity scattering are also included in the model. Our calculations reveal that by changing the characteristics of the grains, such as their potential barrier height and size, one can increase the mean energy per carrier and obtain an optimum power factor for improved thermoelectric performance. The model is successfully applied to explain experimental data for PbTe nanocomposites. We also discuss the importance of various material dependent electronic structure parameters for the relevant transport properties in other

thermoelectric nanocomposites.

4:15 PM N5.9

Enhancement of the Thermoelectric Figure of Merit in the Gated Bismuth Telluride Nanowires. Igor Bejenari¹, Valeriu Kantser² and Alexander A Balandin¹; ¹Electrical Engineering and Materials Science and Engineering, University of California - Riverside, Riverside, California; ²Institute of Electronic Engineering & Industrial Technologies, ASM, Kishinev, Moldova.

Nanostructured materials offer potential for improving the thermoelectric figure of merit and efficiency of the thermal-to-electric energy conversion [1]. In this talk we show that a combination of the quantum confinement effects in bismuth telluride quantum wires with properly applied electric bias can increase the thermoelectric power conversion by an order of magnitude. As an example system we considered square cross-section bismuth telluride quantum wires grown along [110] direction [2]. The coupled Schrodinger - Poisson equations were solved self-consistently using the trigonometric functions and Gauss - Lobatto - Legendre interpolating polynomials as the basis function elements. At small values of the gate bias the Poisson's equation was solved analytically by using the Thomas - Fermi approximation. In this case, the solution of the Schrodinger equation was expressed by the Mathieu functions. In the framework of our theoretical model we obtained the dependence of the thermoelectric parameters on the gate voltage as well as on the space variables. It was found that the electric field effect is significant when the quantum wire thickness is less or comparable to the electron Debye screening length. Under applied positive (negative) gate bias the electron (hole) contribution to the thermoelectric power of the intrinsic quantum wires becomes dominant. In nanowires of medium thickness (15 nm) the transverse electric field increases concentration of both types of carriers while in narrow nanowires (7 nm) it increases the concentration of only type of carriers depending on the gate polarity. We have established that both the dimensional confinement and electric field effects lead to the reduction of the nanowire thermal conductivity. The Seebeck coefficient can be increased by a factor of two in nanowires of 7 nm diameter. The overall electric-field effect results in the enhancement of the thermoelectric figure of merit by an order of magnitude. The enhancement is larger for the positive gate bias because the electron mobility exceeds that of the holes. The obtained results may lead to a new method of improving the thermoelectric figure of merit for more efficient thermal-to-electric energy conversion. IB acknowledges the Fulbright Program grant to conduct research at NDL. The work in Balandin group was supported in part through the DARPA UCR - UCLA - UCSB Center for Nanoscience Innovations for Defense (CNID). [1] A.A. Balandin and O.L. Lazarenkova, Mechanism for thermoelectric figure-of-merit enhancement in regiminated quantum dot superlattices, Appl. Phys. Lett., 82, 415 (2003). [2] I. Bejenari and V. Kantser, Thermoelectric properties of bismuth telluride nanowires in constant relaxation time approximation, Phys. Rev. B 78, 115322 (2008).

4:30 PM N5.10

Tailoring Interface Roughness and Superlattice Period Length in Novel Electron Filtering Thermoelectric Materials. Shidong Wang¹ and Natalio Mingo²; ¹LETI/DRT/D2NT/LNDE, CEA-Grenoble, Grenoble, France; ²LITEN, CEA-Grenoble, Grenoble, France.

We quantify the effects of interface roughness and superlattice period on thermoelectric electron filtering [1,2] in superlattices, using the non-equilibrium Green's function method with a realistic description of the interface. In contrast with previous suggestions, we find that rough interfaces do not enhance the power factor more than smooth ones. Electron filtering does not increase the thermoelectric power factor if the well length is longer than the inelastic mean free path. Quantitative results are provided in the case of InGaAs/InAlGaAs superlattices[3]. 1. D. Vashaee, & A. Shakouri, J. Appl. Phys. 95, 1233-1245(2004); 2. D. Vashaee, & A. Shakouri, Phys. Rev. Lett. 92, 106103(2004); 3. S. Wang, & N. Mingo, to be published.

SESSION N6: Bulk Materials I
Chairs: Thierry Caillat and Hiromichi Ohta
Thursday Morning, April 16, 2009
Room 2010 (Moscone West)

8:30 AM N6.1

Double-Filled Skutterudites: $\text{Sr}_y\text{Yb}_x\text{Co}_4\text{Sb}_{12}$, $\text{Ca}_y\text{Yb}_x\text{Co}_4\text{Sb}_{12}$, and $\text{Ce}_y\text{Sr}_x\text{Co}_{4-z}\text{Fe}_{4-z}\text{Sb}_{12}$, Synthesis and High Temperature Transport Measurements. James R. Salvador¹, Jihui Yang¹, Xun Shi¹ and Hsin Wang²; ¹Materials and Processes Lab, GM R&D center, Warren, Michigan; ²Materials Science and Technology Division, Oak Ridge National Lab, Oak Ridge, Tennessee.

In this work we explore several different combinations of filling atoms from the alkaline earth metal and rare earth metal groups. It has been shown theoretically and experimentally that filling the crystallographic voids in the skutterudite structure with elements from different chemical groups such as: alkaline earths, rare earths, or alkali metals can more effectively reduce the thermal conductivity by scattering a wider frequency range of phonons as compared to materials with one type of filler. Work dealing with Yb and Ba filling has been presented before, and here we expand upon these initial findings to include $\text{Sr}_y\text{Yb}_x\text{Co}_4\text{Sb}_{12}$, $\text{Ca}_y\text{Yb}_x\text{Co}_4\text{Sb}_{12}$, and $\text{Ce}_y\text{Sr}_x\text{Co}_{4-z}\text{Fe}_{4-z}\text{Sb}_{12}$. Interestingly, not all combinations of filler ions can be incorporated into the skutterudite structure. We will also discuss combinations which are not thermodynamically stable. In addition we present aspects of sample preparation and processing that are vital in obtaining high quality and high ZT materials. The work is in part supported by GM, by DOE under corporate agreement DE-FC26-04NT42278, by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies as part of the High Temperature Materials Laboratory User Program at Oak Ridge National Laboratory managed by the UT-Battelle LLC, for the Department of Energy under contract DE-

AC05000OR22725.

8:45 AM N6.2

Preparation and Fundamental Properties of Clathrate-II Intermetallic Phases: Materials with Potential for Energy Conversion Applications. Matt Beekman and George S Nolas; Department of Physics, University of South Florida, Tampa, Florida.

Intermetallic clathrate compounds have generated a great deal of interest as potential candidates for thermoelectric power generation applications, owing predominantly to the very low thermal conductivity that can be achieved by suppression of the lattice thermal conduction by inclusion of "rattling" guest species. The interest continues to thrive in part due to the vast compositional variety possible within single structure types. This is particularly true of the clathrate-II structure type, which also exhibits potential for very low thermal conductivity, in which the guest content may also be readily varied, but for which only a small number of compositions have been investigated to date. Fundamental understanding of the properties of these materials has a direct impact on their implementation in energy conversion applications. We present recent results from an ongoing fundamental study on the synthesis, structural, and physical properties of group 14 based clathrate-II materials. Evidence is presented that the guest-framework interaction is strongly dependent upon local coordination of the guest and/or relative guest/cage size, with the NaxSi_{136} ($0 < x < 24$) clathrates as a paradigm. In addition to recent results in characterization, opportunities for novel synthetic routes to intermetallic clathrates as well as new compositions will be highlighted, and the potential these materials possess for thermoelectric applications will also be discussed.

9:00 AM *N6.3

The Thermoelectric Potential of Inverse Clathrates. Peter Franz Rogl¹, Matthias Falmbigl¹, Ernst Bauer², Andrij Grytsiv¹, Herwig Michor², Esmaeil Royanian^{1,2} and Gerald Giester³; ¹Institute of Physical Chemistry, University of Vienna, Wien, Austria; ²Institute of Solid State Physics, Vienna University of Technology, Wien, Austria; ³Institute of Mineralogy and Crystallography, University of Vienna, Wien, Austria.

Formation, crystal chemistry and physical properties were investigated for novel inverse clathrates deriving from $\text{Sn}_{19}\text{Cu}_4\text{P}_{22}\text{I}_8$. Substitution of Zn, In, Ag, Au was attempted to bring down electrical resistivity at low thermal conductivity. The phase region of the clathrate phases was determined from metallography, EMPA and X-ray diffraction data. Structural investigations for all specimens confirm isotypism with the cubic primitive clathrate type I structure (space group type $\text{Pm}\bar{3}\text{n}$). Mechanical properties (hardness, shear modulus etc.) will be compared to type I clathrates. Temperature dependent X-ray spectra and the heat capacity define a low-lying, almost localized, phonon branch. Studies of transport properties evidence holes as the majority charge carriers in this system. The thermoelectric potential (physical properties) of the entire class of inverse clathrates is discussed in detail.

9:30 AM N6.4

Novel Type-I Clathrates with Tunable Band Gap Xun Shi¹, James R Salvador¹, Jihui Yang¹, Jiong Yang², Wenqing Zhang², Lidong Chen² and Hsin Wang³; ¹Materials & Processes Lab, General Motors R&D center, Warren, Michigan; ²State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China; ³Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Advanced semiconductor technology requires materials with different band gaps for various applications. Type-I clathrates are promising novel semiconducting materials for thermoelectric applications in the temperature range of 700 K to 1000 K. We report the chemical and structural analysis, and electrical and thermal transport properties of transition metal doped clathrates. Our data show that these clathrates are narrow band gap semiconductors. Based on these results, a series of novel type-I clathrates are predicted and prepared, and the thermoelectric properties are measured from low to high temperature. A tunable band gap is observed in these materials through modifying the chemical composition. These novel tunable narrow gap clathrates suggest potential applications in thermoelectrics and other semiconductor industry.

9:45 AM N6.5

Enhanced High-Temperature Thermoelectric Performance of $\text{Yb}_{14-x}\text{Ca}_x\text{MnSb}_{11}$ Catherine A. Cox¹, Eric S Toberer², Shawna R Brown¹, G. Jeffrey Snyder² and Susan M Kauzlarich¹; ¹Department of Chemistry, University of California, Davis, California; ²Materials Science, California Institute of Technology, Pasadena, California.

The Zintl phase, $\text{Yb}_{14}\text{MnSb}_{11}$, is a good candidate for high temperature efficient thermoelectric power generation because of its complex structure and the ability to tune the electronic properties through chemical substitution. In 2006, the p-type material $\text{Yb}_{14}\text{MnSb}_{11}$ was discovered to have a max $zT = 1.0$ at 1200 K. Substitution of Zn^{2+} or Al^{3+} for the Mn ion and La^{3+} for Yb^{2+} has resulted in improved thermoelectric properties by reduction of spin-disorder scattering or by means of optimization of carrier concentration. Here, we describe the effect of isoelectronic substitution of Ca^{2+} for Yb^{2+} on the thermal conductivity. Solid solutions, $\text{Yb}_{14-x}\text{Ca}_x\text{MnSb}_{11}$, $1 \leq x \leq 8$, were synthesized via Sn-flux in order to determine the composition with the optimum thermoelectric properties. Composition was determined by single-crystal X-ray diffraction and phase purity analyzed by powder X-ray diffraction. High temperature thermoelectric properties were measured and will be presented.

10:30 AM *N6.6

Resonant Impurity Levels can Enhance the Thermoelectric Figure of Merit. Joseph P Heremans, Department of Mechanical Engineering, Ohio State University, Columbus, Ohio; Department of Physics, Ohio State University, Columbus, Ohio.

It was shown in 2008 that thallium-doped PbTe can have a thermoelectric figure of merit twice that of similarly p-type doped material, reaching $zT=1.5$ at 775K [1], via an enhancement in Seebeck coefficient for a given carrier concentration. These results are consistent with the Mahan and Sofo [2] theory, which predicts how solids in which the electronic density of states (DOS) displays a narrow maximum as a function of energy E can display a strong enhancement in power factor. This talk will first review the experimental results in PbTe:TI. It will then provide experimental evidence that the zT -enhancement is indeed related to the local increase in DOS, as opposed to being related to a complementary theory by Ravich [3] based on the scattering mechanisms. The criteria for zT -enhancement by resonant levels will be presented, and the prospects of discovering such levels in other thermoelectric semiconductor systems will be discussed. [1] J. P. Heremans et al., Science 321 554 (2008) [2] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. U.S.A. 93, 7436 (1996). [3] Y. I. Ravich et al., Proc. IX Int. Conf. on Thermoelectrics (USA), C. B. Vining, Ed., JPL, Pasadena, p. 278 (1990)

11:00 AM N6.7

Ternary Copper-Based Diamond-Like Semiconductors for Thermoelectric Applications Donald Morelli and Eric Skoug; Chemical Engineering & Materials Science, Michigan State University, East Lansing, Michigan.

Ternary semiconductors possessing a nominal valence of four electrons per atom can be built up from the diamond-structure III-V and II-VI and rocksalt-structure IV-VI semiconductor families. Very well known examples are: i) the chalcopyrite structure compounds, derived from a doubling of the unit cell of the II-VI structure and replacing the two divalent cations with one monovalent and one trivalent cation to create the I-III-VI₂ family, e.g., CuGaSe₂; and ii) the rocksalt-like structures derived from a doubling of the unit cell of the IV-VI structure and replacing the two divalent cations with one monovalent and one trivalent (group V) cation to create the I-V-VI₂ family, e.g. AgSbTe₂. Less well known are higher order Cu- and Ag-based semiconductors that follow from the transformations $3(\text{II}+\text{VI}) \rightarrow (\text{I}2+\text{IV})+\text{VI}3$ (e.g. Ag₂GeSe₃) and $4(\text{II}+\text{VI}) \rightarrow (\text{I}3+\text{V})+\text{VI}4$ (e.g. Cu₃SbSe₄). In light of the interesting thermoelectric properties of the I-V-VI₂ phase compounds, we have sought similar behavior in the higher-order compounds described above. In this talk we present some preliminary results on the thermoelectric properties of a host of ternary diamond-like and rocksalt-like semiconducting compounds.

11:15 AM N6.8

Is Tin a Resonant Level in Bismuth Telluride? Christopher M Jaworski¹, Vladimir Kulbachinskii² and Joseph P Heremans^{1,3}; ¹Department of Mechanical Engineering, The Ohio State University, Columbus, Ohio; ²Low Temperature Physics Department, Physics Faculty, Moscow State University, Moscow, Russia; ³Department of Physics, The Ohio State University, Columbus, Ohio.

Kulbachinskii and co-workers[1] report that Sn might form a resonant level in Bi₂Te₃, and the present study is to investigate whether Sn can enhance its zT . Single crystals of Bi₂-xTe₃Sn_x have been grown in the range $x=0-0.3$. Electrical resistivity, Seebeck, Hall, and transverse Nernst-Ettingshausen coefficients of the crystals have been measured in the temperature range 77-400 Kelvin. From these we calculate Fermi Energy, carrier density, carrier mobility, density of states effective mass, and scattering exponent[2]. Shubnikov de Haas measurements were performed at 2K thus yielding Fermi surface areas and 2K carrier densities. We present a Seebeck coefficient versus carrier density relation (Pisarenko plot), as ascertained from literature and confirmed in this experiment. The addition of tin is seen to increase resistivity above that of pure Bi₂Te₃ below 250 K and decrease it above. We also see a reduction in the Nernst coefficient with increasing tin concentration. 1. V. A. Kulbachinskii et al., Phys. Stat. Sol. 199 505 (1997) 2. J. P. Heremans et al., Phys. Rev. B 70, 115334 (2004).

11:30 AM N6.9

The Effect on Thermoelectric Properties of Cd Substitution in PbTe. Kyunghan Ahn¹, Mi-Kyung Han¹, Huijun Kong², Ctirad Uher² and Mercouri G Kanatzidis¹; ¹Chemistry, Northwestern University, Evanston, Illinois; ²Physics, University of Michigan, Ann Arbor, Michigan.

Thermoelectric (TE) power generation is the focus of considerable attention because of the potential for environmentally benign and cost-effective conversion of waste heat to electricity. A recent theoretical study showed that a significant enhancement in the electronic density of states (DOS) can be achieved when Cd is introduced on the metal sites of the PbTe rock salt structure. The substitution of Cd in PbTe can result in a distortion in the DOS near the bottom of the conduction band and thus cause an enhancement in the Seebeck coefficient. In this study we explored the effect of Cd doping on TE properties of PbTe in an effort to test the theoretical predictions. More importantly, the appropriate level substitution of Cd for Pb in PbTe was explored. We present detailed investigations of structural and spectroscopic data as well as transport properties including electrical conductivity, Seebeck coefficient, Hall effect, and thermal conductivity data on samples of Pb_{1-x}Cd_xTe ($x = 0.01, 0.03, 0.05, 0.07$, and 0.10). An enhancement in zT is observed and its origin will be discussed.

11:45 AM N6.10

Thermoelectric Properties of Spark Plasma Sintered Re₃As_{7-y}(Si,Sn)_y. Tim Holgate¹, Terry M Tritt¹, Holger Kleinke², Hong Xu² and Jian He¹; ¹Clemson University, Clemson, South Carolina; ²University of Waterloo, Waterloo, Ontario, Canada.

Like the competitive thermoelectric material $\text{Mo}_3\text{Sb}_{5.4}\text{Te}_{1.6}$ ($ZT \sim 0.8$ at 1000K)^[1], Re_3As_7 is an Ir_3Ge_7 -type metallic structure that can be rendered a narrow bandgap semiconductor by partial substitution of As with Si or Sn. This results in a favorable band structure for thermoelectric materials. Furthermore, the effect of interstitial doping of transition metal ions (Co, Fe, Ni) on the band structure and thermal conductivity is also of interest, as such doping of 6% Ni into $\text{Mo}_3\text{Sb}_{5.4}\text{Te}_{1.6}$ resulted in an increase of ZT to about 0.96 at 1000K.^[1] Additionally, the effect of processing by spark plasma sintering versus hot isostatic pressing has been made. The thermoelectric properties of $\text{Re}_3\text{As}_{7-y}(\text{Si},\text{Sn})_y$ and its potential as an n-type counterpart to the p-type $\text{Mo}_3\text{Sb}_{7-y}\text{Te}_y$ have been investigated and are presented herein. ^[1]H. Xu, N. Soheilnia, H. Zhang, T. M. Tritt and H. Kleinke, Mat. Res. Soc. Proc., 2008, U11-02

SESSION N7: Applications, Devices, and Metrology

Chair: Tim Hogan

Thursday Afternoon, April 16, 2009

Room 2010 (Moscone West)

1:30 PM **N7.1**

Abstract Withdrawn

2:00 PM **N7.2**

Manufacturing Optimally-Sized Thermoelectric Elements Through Self Assembly. James Tuckerman, Gary Hendrick and Nathan B Crane; Mechanical Engineering, University of South Florida, Tampa, Florida.

While thin film thermoelectric cooling looks very promising in first-order analysis, parasitic effects significantly degrade their performance. Recent developments in bulk nanostructured materials promise improved material performance parameters. However, for optimal performance, they must be combined in sub-millimeter thicknesses that are not achievable using traditional approaches such as manual, robotic, or vibratory feeding. In this work, self-assembly is demonstrated to provide a feasible alternative. A method is presented for the self-assembly of 500 micron thermoelectric elements using capillary forces into arrays of alternating N and P type elements through a two-stage assembly process. This method is shown to be applicable to smaller sized elements as well. Potential mechanism for material degradation during processing are addressed. Preliminary measurements of device performance are reported. The impact of potential self-assembly errors such as missing components on thermoelectric performance are assessed through Monte Carlo simulation. The simulations show that process modifications can significantly improve device performance. The simulations are based on 1-D models that include the effects of thermal contact resistance, electrical contact resistance and filler material between the p and n type of thermoelectric materials.

2:15 PM **N7.3**

Bi_2Te_3 as a Low Temperature Seebeck Coefficient Standard Reference Material (SRM™) Winnie Wong-Ng¹, Nathan D Lowhorn¹, Evan L Thomas¹, Qing Huang², John Lu³, Makoto Otani¹, Martin L Green¹, Wai-Yim Ching⁴, Thanh N Tran⁵, Jeffrey Sharp⁶ and Neil R Dille⁷; ¹MSEL, NIST, Gaithersburg, Maryland; ²NCNR, NIST, Gaithersburg, Maryland; ³Statistical Engineering Division, NIST, Gaithersburg, Maryland; ⁴Physcis Department, University of Missouri, Kansas City, Missouri; ⁵Power Sources R&D, Naval Surface Warfare Center, Bethesda, Maryland; ⁶Materials R&D, Marlow Industries, Dallas, Texas; ⁷Quantum Design, San Diego, California.

The discovery of novel thermoelectric materials with relatively high ZT offers the potential for higher conversion efficiency in both power generation and cooling applications. In an effort to expedite research efforts in the thermoelectrics field, we have developed a Seebeck coefficient (or thermopower) standard reference material (SRM™). Based on the round-robin survey that we conducted in last year, Bi_2Te_3 has been chosen as the prototype low temperature Seebeck coefficient SRM. These SRM samples are in the form of bars with dimensions of $3.5 \times 2.5 \times 8 \text{ mm}^3$. We have completed the certification process using two different measurement techniques. This talk will discuss the Seebeck coefficient measurements, statistical analysis and further characterizations that include resistivity measurements, and temperature dependent structural analysis using neutron diffraction, etc.

2:30 PM **N7.4**

High Temperature Bulk Thermoelectric Properties on a Single Specimen: A Study of Microstructure and Material Homogeneity Hsin Wang¹, James R Salvador², Xun Shi² and Jihui Yang²; ¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²R&D Center, General Motors, Warren, Michigan.

Bulk thermoelectric materials are candidates for automotive waste heat power generation. One must obtain accurate figures of merit over the automotive exhaust heat temperature range (300K - 800K) to ensure realistic and predictable estimates for power generation. These estimates can be compromised if inhomogeneous samples are used for property measurements. This study focuses on the influence of material homogeneity and microstructure on transport properties. In most high temperature studies, thermal and electrical transport properties are measured separately on two different specimens. The assumption is the material is uniform in composition and has the same microstructure. However, this may not be the case in research materials prepared by various processing methods. Significant errors in ZT calculations can occur if measurements are conducted on two specimens with composition and microstructure differences. We prepared skutterudite and lead telluride cylinders by the spark plasma

sintering (SPS) method whose dimensions were 10 mm length and 12.7 mm diameter. Multiple thin disk specimens were cut from the cylinders. Thermal transport and electrical properties were measured on the same specimen. The variations of transport properties are presented and discussed.

2:45 PM **N7.5**

Survey of High Temperature Thermoelectric Metrology. Joshua Martin and Winnie Wong-Ng; National Institute of Standards and Technology, Gaithersburg, Maryland.

The rapid increase in thermoelectric (TE) materials R&D is a consequence of the growing need to increase energy efficiency and independence through waste heat recovery. TE materials enable the direct solid-state conversion of heat into electricity, with little maintenance, noise, or cost. The conversion abilities of these materials are effectively compared through the figure of merit, $ZT = S^2 \sigma T / \kappa$, where T is the temperature, σ and κ are the measured electrical and thermal conductivity, respectively, and S is the Seebeck coefficient, a ratio of the emergent voltage per temperature difference. Current Seebeck coefficient measurement apparatus employ a variety of methodologies and techniques. However, no standardization exists to ensure reliable inter-laboratory confirmation of reported characterizations. To address these challenges and to stimulate broad discussion into advancing thermoelectric characterization at elevated temperature (>300K), NIST is currently developing an apparatus capable of evaluating these disparate characterization methodologies with minimal uncertainty. This talk will provide a non-exhaustive overview of high temperature thermoelectric metrology apparatus and methods, including a discussion on techniques to minimize critical uncertainties.

SESSION N8: Bulk Materials II

Chair: Yuri Grin

Thursday Afternoon, April 16, 2009

Room 2010 (Moscone West)

3:30 PM ***N8.1**

Thermal Conductivity Reduction Paths in Thermoelectric Materials. Claude Godart, Semiconductors and Nanomaterials for Energy and Environment, CNRS, Thiais, France.

The figure of merit $ZT = \sigma S^2 T / \kappa$ (S the Seebeck coefficient, σ and κ the electrical and thermal conductivity respectively) is an essential element of the efficiency of a thermoelectric material for applications, which convert heat to electricity or, conversely, electric current to cooling. From the expression of the power factor $\sigma S^2 T$ it was deduced that a highly degenerated semiconductor is necessary. In order to reduce the lattice part of the thermal conductivity, various mechanisms were tested in new thermoelectric materials and had been the topics of different reviews. These include cage-like materials, effects of vacancies, solid solutions, complex structures (cluster, tunnel, ...), nano-structured systems. We plan to review such aspects in the modern thermoelectric materials and include results of the very last years in such view. Moreover, as micro- and nano-composites seem to be promising to increase ZT in large size samples, we will also briefly discuss the interest of spark plasma sintering technique to preserve the micro- or nano- structure in highly densified samples.

4:00 PM **N8.2**

Thermoelectric Properties of $\text{In}_x\text{Yb}_y\text{CoSb}_3$ (x and $y = 0 \sim 0.2$) Double-filled Skutterudite. Jiangying Peng^{1,2}, Zhe Su¹, Pola Alboni¹, Song Zhu¹, Jian He¹ and Terry M Tritt¹; ¹Department Physics and Astronomy, Clemson University, Clemson, South Carolina; ²School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei, China.

The double-filling approach has proved to be effective in reducing the lattice thermal conductivity and in turn improving the thermoelectric performance of CoSb_3 -based skutterudite. In this study we report the results of (In, Yb) -filled CoSb_3 samples. The samples with general formula $\text{In}_x\text{Yb}_y\text{CoSb}_3$ (x and $y = 0, 0.05, 0.10, 0.15, 0.20$, respectively) were prepared using a melting-sintering method, and have been studied by mean of the Seebeck coefficient, electrical resistivity, and thermal conductivity measurement as a function of temperature from room temperature up to 900 K. The Hall effect and microscopy study provide extra insights into the effects of filling. A dimensionless figure of merit ZT value of 1 has been attained in $\text{In}_{0.2}\text{Yb}_{0.1}\text{CoSb}_3$ at 700K, while promising thermoelectric performance has been found in other compositions.

4:15 PM **N8.3**

Bridgman Growth and Electrical Characterization of PbTe. Biplab Paul and Pallab Banerji; Materials Science Centre, Indian Institute of Technology, Kharagpur, West Bengal, India.

Lead telluride (PbTe) has some unique properties like positive temperature coefficient, smaller Auger recombination rate, etc. and due to its high carrier mobility and low thermal conductivity it has much potential in thermoelectric applications. In this present communication we report the growth of p-type PbTe single crystal by vertical Bridgman method without using any seed. The structural properties were obtained from the X-ray analysis of the samples. All the diffraction peaks of the powdered sample correspond to PbTe crystal with lattice constant 6.542 Å. Absence of peaks due to Pb and Te or any other phase except PbTe in the XRD pattern of the powdered sample confirms the proper synthesis of the compound has been occurred. The wafer sliced from the ingot contains only one peak in <220> direction. Being with the preferred orientation along <220> direction, we conclude that the wafer is single crystal. The dislocation density of the crystal was measured from the calculation of etch pit obtained on

mechanically and chemically etched surface of wafer. A dislocation density in the range 10^4 - 10^5 cm⁻² was found. The band gap was measured from a thin film, deposited from the as grown crystal. From the intercepts of the extrapolation of the linear portion of $(\hbar\nu)^{1/2}$ vs $\hbar\nu$ plot on the energy axis we obtained the indirect energy band gap of 0.292 eV. Hot probe measurements showed that the samples were p-type. The resistivity and Hall mobility of the wafers, one sliced from the upper part of the ingot (A) and another sliced from the lower part of the ingot (B) were determined by Vander Pauw technique in the temperature range 100-300 K. The resistivities in general indicated the semimetallic nature decreasing from 300 - 100 K by approximately a factor of 10. The resistivity of "A" is higher than that of "B" for all the temperatures. This variation of resistivity may arise from the lattice imperfection developed during single crystal growth. Hall coefficient is nearly constant over the entire temperature range from 100-300 K and this behavior, also observed in many other semiconductors, may be due to the overlapping of the broadened impurity band with the adjacent valence band. The values of the Hall coefficient correspond to hole concentration of the order of 10^{17} cm⁻³. This high value of hole concentration may probably arise due to deviations from stoichiometry instead of presence of impurities because of special care taken during crystal growth. The concentration of hole remains almost constant throughout the entire temperature range covered implying that extrinsic centre ionization energy E_i vanishingly small and intrinsic carrier is not large enough to influence the conduction process. Hydrogenic impurity model also support this small value E_i for the compounds with large dielectric constant. The mobility was found to vary with temperature according to $\mu \sim T^{-n}$ in the temperature range of covered with $n = 2.77$.

4:30 PM N8.4

Structural Analysis of PbTe- and GeTe-Based Thermoelectric Materials by ¹²⁵Te NMR Evgenii M Levin^{1,2}, Bruce A Cook¹, Rama Venkatasubramanian³ and Klaus Schmidt-Rohr^{1,4}; ¹Ames Laboratory Division of Materials Sciences & Engineering, Iowa State University (ISU), Ames, Iowa; ²Dept. of Physics and Astronomy, ISU, Ames, Iowa; ³RTI International, Research Triangle Park, North Carolina; ⁴Dept. of Chemistry, ISU, Ames, Iowa.

Several types of multicomponent tellurides have been explored intensely as promising thermoelectric materials with high figures of merit, ZT. Nanostructuring in bulk thermoelectrics has been pursued as a means of reducing thermal conductivity by phonon scattering while retaining high electrical conductivity [1]. However, it remains to be shown to what extent bulk materials can be engineered or modified to approach the theoretical, ideal structures. To achieve this goal, reliable high-resolution probes of the chemical and electronic structure of tellurides are needed. We show here that high-resolution ¹²⁵Te NMR is such a technique, being able to provide new insights into the chemical structure and charge carrier concentration of complex telluride-based thermoelectrics. The peak position in NMR of semiconductors reflects (i) chemical bonding (chemical shift) and (ii) the free carrier concentration (Knight shift). ¹²⁵Te magic-angle spinning NMR spectra of PbTe and GeTe show distinct peak positions of -1750 vs. +250 ppm and linewidths of 4.5 vs. 49 kHz, respectively. This is evidence that Te in these compounds has different bonding and local symmetry. In PbTe, additions of Sb and Ag (e.g., "LAST" compositions) produce a distinct secondary ¹²⁵Te NMR band, while similar additions in GeTe-based "TAGS" samples result in an overall shift and broadening of the spectral band. Furthermore, measurements of the spin-lattice relaxation time, T₁, enable determination of the local charge carrier concentration [2]. The T₁ relaxation in GeTe and TAGS can be fitted by one contribution with T₁ ~ 4 ms, while the relaxation in several LAST materials is biexponential and can be fitted by two contributions with fractions of A~0.7, B~0.3, and T_{1,A}, T_{1,B} differing by almost a factor of 10. These values imply the existence of two phases, each possessing distinct charge-carrier concentrations differing by an order of magnitude, within a given sample. While many PbTe-based materials are electronically inhomogeneous, there is no such evidence for GeTe. The electronic inhomogeneities observed in LAST materials suggest the presence of multiple phases within a given sample, consistent with the concept of nanostructuring, which is expected to affect the electronic and thermal conductivities, and ultimately ZT. [1] K.F. Hsu, et al. Science, 303, 818 (2004). [2] Alexander et al., J. Nonmetals 1, 251 (1973).

4:45 PM N8.5

Effects of Processing Parameters on Microstructure and Thermoelectric Properties of Bismuth Telluride Alloys Synthesized with Spark Plasma Sintering (SPS). Nancy Yang¹, Michael Morita¹, Alf Morales¹, Peter A Sharma¹, Miles Clift¹, Zhihui Zhang², Yizhang Zhou² and Enrique J Lavernia²; ¹Sandia National Laboratories, Livermore, California; ²Department of Chemical Engineering and Materials Science, University of California, Davis, Davis, California.

Thermoelectric properties of polycrystalline Bi₂Te₃ materials greatly depend on their microstructures including grain sizes, grain orientations, grain boundaries, porosities, and so on. In this work, the synthesis, microstructure and thermoelectric property relationship in Bi₂Te₃ disks, sintered using spark plasma sintering (SPS) techniques, were studied by employing different powder sizes (e.g. 10 µm and 100 µm) and a variety of sintering temperatures (320-440 °C) and pressures (10-80 MPa). The sintered Bi₂Te₃ alloys exhibited highly preferred (001) orientations along the loading axis with different level of porosity (1-12%). The effect of particle size, grain size, sintering temperature and pressure on the thermoelectric properties are discussed.

SESSION N9: Novel Oxides
Chairs: Donald Morelli and Jihui Yang
Friday Morning, April 17, 2009
Room 2010 (Moscone West)

8:30 AM N9.1

Thermoelectric Zintl Compounds in R-T-Sb (R = Ba, Eu, Yb; T = Zn, Cd) Systems. X. J Wang¹, H. Zhang¹, M. B Tang¹, X. X Yang¹, H. H Chen¹, Z. Y Man¹, U. Burkhardt², Jing-tai Zhao¹ and Y. Grin²; ¹Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China; ²Max Planck Institute for Chemical Physics of Solids, Dresden, Germany.

Recently many new promising thermoelectric (TE) materials have been found in a special category of intermetallic compounds, i.e. Zintl phases. The classical Zintl phases are semiconductors with narrow band gap and many have complex crystal structures containing "rattle" heavy atoms to produce low lattice thermal conductivities. In our systematic investigations of potential TE materials in intermetallic compounds with polar character, ternary Zintl phases $RxTySz$ ($R=Ba, Yb$ and Eu ; T =Transition elements; S = Semi-metal elements) showed to be promising. Based on first principle calculations on electronic structures and crystal structure analyses, the pnictide candidates such as $BaZn_2Sb_2$, $YbCd_2Sb_2$ and $EuCd_2Sb_2$ were synthesized and their thermal and electrical transport properties were characterized. These compounds show promising TE properties with considerably high figure of merit (e.g. $ZT \sim 1$ at 700K for $YbCd_2Sb_2$). The solid solution system $YbCd_xZn_{2-x}Sb_2$ ($x = 0, 0.4, 0.8, 1, 1.2, 1.6$ and 2) were synthesized and their TE properties were also characterized. The results revealed that Zn substitution of Cd in $YbCd_2Sb_2$ can easily tune carrier concentration and decrease thermal conductivity, which resulted in improvement of ZT value (e.g. $ZT \sim 1.2$ at 700K for $x = 0.4$).

8:45 AM **N9.2**

High-temperature Thermoelectric Performance of $Sr_{1-x}La_xTiO_{3-d}$, Matthew L Scullin^{1,2}, J. Ravichandran^{2,4}, S. Mukerjee^{2,3}, Y. Koh⁶, D. Cahill⁶, J. Moore^{2,3}, A. Majumdar^{2,5} and R. Ramesh^{1,2,3}, ¹Materials Science and Engineering, University of California, Berkeley, Berkeley, California; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California; ³Physics, University of California, Berkeley, Berkeley, California; ⁴Applied Science and Technology, University of California, Berkeley, Berkeley, California; ⁵Mechanical Engineering, University of California, Berkeley, Berkeley, California; ⁶Materials Science and Engineering, University of Illinois - Urbana, Urbana, Illinois.

We report the thermoelectric performance of doubly-doped strontium titanate, $Sr_{1-x}La_xTiO_{3-d}$, in the temperature range 300-1000K. Power factor* T in this n-type oxide semiconductor is large (> 1 W/m-K @300K) due to the enhanced effective mass of electrons from oxygen vacancy doping and high carrier concentrations from lanthanum doping, and increases to 1.6 W/mK @ 500K for some doping levels. Thermal conductivity is also four times lower in these thin-films versus bulk, yielding zT values greater than 0.5 at typical engine exhaust gas temperatures (300-600°C). These attractive high-temperature properties make this material a strong competitor for use in thermoelectric waste heat recovery.

9:00 AM ***N9.3**

Why Do Layered Cobaltates Have Good Thermoelectric Properties? Rongying Jin, Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee.

Layered cobaltates are ideal systems for studying low-dimensionality effects on thermoelectric performance of bulk samples, as they naturally form superlattice structures. By investigating the anisotropy of thermoelectric properties of $NaxCoO_2$ and $Ca_3Co_4O_9$ single crystals and by comparing these quantities with that obtained from other layered and correlated electron materials, we argue that good thermoelectric properties in these systems are due to their unique crystalline structure and chemical compositions. This is further supported by the results obtained from a series of $Bi_2Sr_2Co_2O_9$ thin films grown in various conditions.

9:30 AM **N9.4**

Abstract Withdrawn

9:45 AM **N9.5**

Mechanical and Thermoelectric Properties of Polycrystalline Na_xCoO_2 Richard Donelson¹, P. H Tsai², Sean Li² and Bryce M Wood¹; ¹Div of Materials Science and Engineering, CSIRO, Clayton, Victoria, Australia; ²School of Materials Science and Engineering, University of New South Wales, Sydney, New South Wales, Australia.

Polycrystalline Na_xCoO_2 ($x \approx 0.7$) is being considered for use as the p-type leg in intermediate temperature thermoelectric generators (TEG). This material exhibits a reasonable thermoelectric performance and is relatively easy to process into useful shapes. In addition to the thermal and electrical properties, a TEG designer will require knowledge of the relevant mechanical properties. Here we report on our efforts to obtain a useful property set for Na_xCoO_2 samples which were produced by solid state reaction.

10:30 AM ***N9.6**

Electric Field Induced Giant Thermopower of Two-dimensional Electron Gas at the Gate Insulator/SrTiO₃ Heterointerface.

Hiromichi Ohta^{1,2}, Akira Yoshikawa¹, Daisuke Kurita¹, Kunihito Koumoto¹, Ryoji Asahi³, Yumi Masuoka³, Kenji Nomura⁴ and Hideo Hosono^{4,5,6}, ¹Graduate School of Engineering, Nagoya University, Nagoya, Japan; ²PRESTO, Japan Science and Technology Agency, Kawaguchi, Japan; ³Toyota Central R&D Laboratories, Nagakute, Japan; ⁴ERATO-SORST, Japan Science and Technology Agency, Yokohama, Japan; ⁵Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; ⁶Frontier Research Center, Tokyo Institute of Technology, Yokohama, Japan.

Two-dimensionally confined electrons in extremely thin layer (thickness < thermal de Broglie wavelength ~ 10 nm), the latter being composed of an electron well and a barrier, exhibit unusually large thermoelectric Seebeck coefficient ($|S|_{2D}$) as compared to the corresponding bulk materials due to the fact that the density of states (DOS) near the bottom of the conduction band increases with decreasing thickness of the electron well^[1]. Recently, we briefly reported that a high density two-dimensional electron gas (2DEG), which was confined within a unit cell layer thickness (0.3905 nm) in SrTiO₃, exhibited a giant $|S|_{2D}$, which was about 5 times larger than that of the bulk SrTiO₃, whereas the 2DEG system retained a rather high σ_{2D} value^[2]. The 2DEG was realized at SrTiO₃/SrTi_{0.8}Nb_{0.2}O₃ superlattices or TiO₂/SrTiO₃ heterointerfaces. To realize 2DEG in a SrTiO₃ crystal, field effect transistor (FET) would be another good way because applying gate voltage accumulates high density conduction electrons within an extremely thin layer at the gate insulator/SrTiO₃ heterointerface^[3]. Here we report unusually large $|S|$ observed in a FET fabricated on SrTiO₃ single crystal surface. (001)-face of SrTiO₃ single crystal plates with stepped & terraced surface were used as active channel. Amorphous LaAlO₃ gate insulating film was deposited on the SrTiO₃ surface at room temperature through the stainless steel mask. Ti metal films were also deposited as source, drain and gate electrodes. $|S|$ values of the channel were measured by conventional steady state method using two thermocouples (K-type). Temperature difference up to 2 K was introduced between the source and the drain electrodes by using two Peltier devices. The σ_{xx} values increased almost proportionally to applied electric field (E) and saturated at 150 μ S. Hall effect measurements revealed that the sheet carrier concentration (n_{xx}) and Hall mobility (μ_{Hall}) values were 4×10^{14} cm⁻² and 2 cm²V⁻¹s⁻¹, respectively. Although $|S|$ values decreased proportionally to $\log E$ when $\sigma_{xx} < 150$ μ S, it dramatically increased with E ($\sigma_{xx} > 150$ μ S). These results indicate that the electron carriers under a high E become two-dimensional conductance in the channel whose thickness is thinner than the thermal de Broglie wavelength (~ 6 nm), resulting in a giant $|S|$ due to the quantum size effect. [1] L. D. Hicks and M. S. Dresselhaus, *Phys. Rev. B* **47**, 12727 (1993). [2] H. Ohta *et al.*, *Nature Mater.* **6**, 129 (2007). [3] K. Ueno *et al.*, *Nature Mater.* doi:10.1038/nmat2298

11:00 AM **N9.7**

New Approach to Improve Figure of Merit in Oxide Thermoelectrics. Venkat Selvamannickam and Bo Zhang; University of Houston, Houston, Texas.

Oxide thermoelectrics are well suited for high-temperature operation since their figure of merit increases even at temperatures of about 1000 K. Also, oxides exhibit excellent stability and oxidation resistance at high temperatures. Furthermore, thermoelectric oxides do not include Pb, Te, Se etc and can be processed in air instead of sealed quartz tube conditions. However, oxide thermoelectrics have not been useful so far because of their relatively lower values of figure of merit. The challenge stems from conflicting performance requirements in thermoelectric materials in general, to achieve high electrical conductivity, but low thermal conductivity while maintaining a high Seebeck coefficient. Seebeck coefficient values of 200 μ V/K has been demonstrated in both p-type and n-type oxides at 800 K, which compare very favorably with those achieved with other thermoelectric materials. High electrical conductivity has also been achieved in oxides, but mainly along the basal plane of single crystals. However, the thermal conductivity of single crystals has not been reduced due to the lack of phonon scattering defects such as grain boundaries, second-phase precipitates, and dislocations. On the other hand, while polycrystalline granular oxides present opportunities to introduce defect structures, their electrical conductivity has been lower because of random grain orientation. In order to address this problem, we are developing novel approaches to achieve a microstructure with an excellent grain alignment of anisotropic thermoelectric oxides along with fine-scale defects such as precipitates, dislocations, and stacking faults to meet the conflicting performance requirements in thermoelectrics. Techniques that have been well proven in oxide superconductors to achieve excellent large-area grain alignment of the high electrical conductivity basal planes are being adopted to oxide thermoelectrics. These techniques simultaneously enable introduction of fine-scale precipitates, dislocations and stacking faults in the grain-aligned structure that can lower thermal conductivity through phonon scattering. Since the basal plane of the anisotropic oxides is the fast growth plane, large areas of the grain-aligned oxides with fine-scale defects can be synthesized. We will report on the process-microstructure-property relationships of the thermoelectric oxides developed by this new approach.

11:15 AM **N9.8**

Transport Properties in Metal Doped In₂O₃ Thermoelectrics. Emmanuel Guilmeau, David Berardan, Charles Simon, Antoine Maignan and Bernard Raveau; CRISMAT laboratory, Caen, France.

Indium oxide is a wide band gap semiconductor which has attracted considerable attention due to its great potential for gas sensing, optical transparency and optoelectronics. Numerous studies have been carried out on thin films of this material as a transparent conductor (TCO). They have shown that the doping with tin increases dramatically the electrical conductivity, as illustrated by the well known Indium Tin Oxide (ITO). More recently, the doping of In₂O₃ with titanium, zirconium, molybdenum or tungsten has shown the possibility to reach exceptionally high carrier mobility with carrier density higher than 10²⁰ cm⁻³ on thin films. Very few attempts have been made to study the transport properties of bulk ceramics of In₂O₃ in view of other applications. Recently, we showed that In₂O₃ bulk ceramics doped with germanium exhibit a great potential as n-type elements for thermoelectric generators for the direct conversion of waste heat into electricity in air at high temperature ($ZT=0.45$ at 1273K). One observes that the conductivity of In₂O₃ is increased by one order of magnitude by Ge doping (0.5 at%) and changes from a semiconducting to a semi-metallic behavior, whereas a high n-type thermopower value is obtained at high temperatures. In order to optimize the thermoelectric properties of such bulk ceramics, it is necessary to study in detail the influence of the nature and concentration of the doping element upon the transport properties of this material. We report in the present study on the substitution of In³⁺ by selected tetra- and pentavalent dopants. Based on accurate Hall effect measurements to determine the

carrier concentration and mobility and XRD analyses of samples, the structural and electrical properties of M4+ and M5+ doped In₂O₃ bulk specimens are described and the influences of the doping metals on the transport properties (within and beyond their solubility limit in the bixbyite structure) are discussed.

11:30 AM N9.9

Abstract Withdrawn

11:45 AM N9.10

Abstract Withdrawn



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Phone: 724 779.3003, Fax: 724 779.8313, Email: [Customer Service](#), [Member Service](#), [Feedback](#)